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ON THE THEORY OF LIQUIDS—IV.

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1. *Introduction.*

The theory which has been discussed in this and preceding papers regards a liquid as being composed of a number of force centres or molecules, each vibrating within an associated spherical space of diameter σ, which is kept free from other molecules by the thermal motion of the occupying molecule. Near the melting point, the translational motion of the molecule through the liquid is assumed to be small compared with the vibratory motion. Each molecule attracts and repels the others with forces varying as inverse powers of the distance. The diameter of a spherical space is calculated assuming that these spaces are closely packed so that σ is taken to vary with temperature being related to V by the equation

$$N\sigma^3 = V\sqrt{2} \qquad (1)$$

In the calculation of properties such as the internal latent heat and surface tension, it can be assumed that each molecule is on an average at the centre of its spherical space, and there need only be considered the attractive force since the repulsive force comes into play at distances less than σ. In the third paper on this subject, an attempt was made to consider the vibratory motion of the molecules and the fractional amplitude of vibration β was linked with the density, internal latent heat of vapourisation, surface tension, viscosity and vapour pressure. Formulæ relating viscosity with surface tension, and vapour pressure with internal latent heat were also obtained. Equations for the coefficient of thermal expansion and compressibility were derived, but only on the assumption that the coefficient of thermal expansion does not vary with temperature.

The formulæ so derived on the whole reproduce satisfactorily the experimental results. In order, however, that the theory should be completely satisfactory, it is necessary that formulæ should be obtained which will give β in terms of the force coefficients, the force indices and the temperature. In the present paper therefore equations have been deduced for the forces on a particle vibrating in a spherical space under the influence of attractive and repulsive forces between that particle and uniformly distributed matter outside the spherical space. It is hoped that the equations derived may also be of interest in the theory of attraction.

2. *Potential Equations.*

In Fig. 1 let a molecule be displaced a distance x from the centre of its sphere 0 to 0′. We assume that the only force acting on the molecular centre is a repulsive force given by λ/r^n, where r is the distance from 0′ to another molecular centre; the effect of the attractive force can be superimposed when the calculations for the repulsive force are completed.

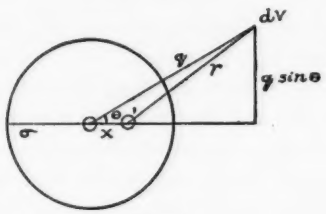

FIG. 1.

The force taken positive for repulsion between the molecular centre at 0′, and the molecules in an annular volume element dV is

$$F = (\lambda N dV)/r^n V \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2)$$

The potential E is given by

$$E = \int_r^\infty F dr \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (3)$$

$$= (\lambda N dV)/[(n-1)\, r^{n-1} V] \quad .. \quad .. \quad .. \quad .. \quad (4)$$

Now we can put (Fig. 1)

$$dV = 2\pi q \sin\theta . dq . q\, d\theta \quad .. \quad .. \quad .. \quad .. \quad .. \quad (5)$$

$$= -2\pi q^2 d(\cos\theta)\, dq \quad .. \quad .. \quad .. \quad .. \quad .. \quad (6)$$

$$= \pi q^2 dB\, dq \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (7)$$

where $B = -2\cos\theta$ .. .. (8)

Hence $E = (k_1 q^2 dB\, dq)/r^s$ .. .. (9)

where $k_1 = (\lambda N \pi)/(n-1) V$ .. .. (10)

and $s = (n-1)$ .. .. (11)

Again $r = (q^2 + x^2 - 2qx\cos\theta)^{\frac{1}{2}}$ .. .. (12)

and $r^{-s} = q^{-s}\{1 + (x^2/q^2)\,[1 - (2q\cos\theta)/x]\}^{-s/2}$ .. .. .. (13)

$$= q^{-s}[1 + c^2(1 + B/c)]^{-s/2} \quad .. \quad .. \quad .. \quad .. \quad (14)$$

where $c = x/q$ .. .. (15)

and is always < 1.

Hence $E = k_1 q^{2-s}[1 + c^2(1 + B/c)]^{-s/2}\, dB\, dq$ .. .. .. (16)

The total potential $\overline{\mathrm{E}}$ of all the surrounding molecules is given by

$$\overline{\mathrm{E}} = \int_{q=\sigma}^{q=\infty} \int_{\substack{\theta=0 \\ \mathrm{B}=-2}}^{\substack{\theta=\pi \\ \mathrm{B}=2}} k_1 \, q^{2-s} \, [1+c^2 \, (1+\mathrm{B}/c)]^{-s/2} \, d\mathrm{B} \, dq \quad .. \quad .. \quad (17)$$

Now $[1+c^2 \, (1+\mathrm{B}/c)]^{-s/2} = 1 + c^2 \, (1+\mathrm{B}/c) \, (-s/2) + c^4 \, (1+\mathrm{B}/c)^2 \, \dfrac{(-s/2)\left(-\frac{s}{2}-1\right)}{1 \, . \, 2}$

$$+ \ldots\ldots$$

$$+ c^{2j} \, (1+\mathrm{B}/c)^j \, \frac{(-1)^j \left(\frac{s}{2}\right) \left(\frac{s}{2}+1\right) \ldots\ldots \left(\frac{s}{2}+j-1\right)}{\underline{|j}}$$

$$+ \ldots\ldots \quad .. \quad .. \quad .. \quad .. \quad .. \quad (18)$$

the $(j+1)$th term being as written.

$$(1+\mathrm{B}/c)^j = 1 + j\mathrm{B}/c + (\mathrm{B}/c)^2 \, \frac{(j) \, (j-1)}{1 \, . \, 2} + \ldots\ldots$$

$$+ (\mathrm{B}/c)^{(2j-l)} \, \frac{(j) \, (j-1) \, (j-2) \ldots\ldots \{j-(2j-l-1)\}}{\underline{|2\,j-l}} + \ldots\ldots \quad .. \quad (19)$$

The coefficient of c^l in the $(j+1)$th term in (18) is therefore

$$(-1)^j \, \mathrm{B}^{(2j-l)} \, \frac{(j) \, (j-1) \, (j-2) \ldots\ldots \{j-(2j-l-1)\} \, (s/2) \, (s/2+1) \ldots\ldots (s/2+j-1)}{\underline{|j} \quad \underline{|2j-l}}$$

.. (20)

$$= \frac{(-1)^j \, \mathrm{B}^{(2j-l)} \, (s/2) \, (s/2+1) \ldots\ldots (s/2+j-1)}{\underline{|2\,j-l} \quad \underline{|l-j}} \quad .. \quad .. \quad .. \quad (21)$$

We may write, therefore,

$$\int_{\mathrm{B}=-2}^{\mathrm{B}=2} [1+c^2 \, (1+\mathrm{B}/c)]^{-s/2} \, d\mathrm{B} = \int_{\mathrm{B}=-2}^{\mathrm{B}=2} [1 + \Sigma\Sigma_{l \; j} \, (21) \, c^l] \, d\mathrm{B} \quad .. \quad .. \quad (22)$$

The range of variation of j will be discussed later.

The integration of (22) gives

$$\left| \mathrm{B} + \sum_l \sum_j (-1)^j \, \frac{\mathrm{B}^{2j-l+1} \, (s/2) \, (s/2+1) \ldots\ldots (s/2+j-1)}{\underline{|2\,j-l+1} \quad \underline{|l-j}} \, c^l \right|_{-2}^{2} \quad .. \quad .. \quad (23)$$

When l is even, $(2j-l+1)$ is odd, and (23) becomes

$$4 + \sum_{\substack{l \\ (\text{even})}} \sum_j \frac{(-1)^j \, 2^{2j-l+2} \, (s/2) \, (s/2+1) \ldots\ldots (s/2+j-1) \, c^l}{\underline{|2j-l+1} \quad \underline{|l-j}} \quad .. \quad .. \quad (24)$$

When l is odd, $(2j-l+1)$ is even and $\Sigma\Sigma$ vanishes for the limits involved.

We now have, from (15), (17) and (24),

$$\overline{\mathrm{E}} = k_1 \int_{q=\sigma}^{q=\infty} \left[4q^{2-s} + \sum_{l\ (\text{even})} \sum_{j} \frac{(-1)^j\ q^{(2-s-l)}\ 2^{2j-l+2}\ \mathrm{D}x^l}{\underline{|2j-l+1}\ \ \underline{|l-j}} \right] dq \qquad .. \quad (25)$$

where $\mathrm{D} = (s/2)\ (s/2+1) \cdot \cdot \cdot \cdot (s/2+j-1)$ .. .. .. (26)

Integrating,

$$\overline{\mathrm{E}} = \frac{4\,k_1}{(s-3)} \cdot \frac{1}{\sigma^{s-3}} + k_1 \sum_{l\ (\text{even})} \sum_{j} \left[\frac{(-1)^j\ 2^{2j-l+2}\ \mathrm{D}x^l}{\sigma^{s+l-3}\ (s+l-3)\ \underline{|2j-l+1}\ \ \underline{|l-j}} \right] \quad .. \quad (27)$$

The work done by the repulsive force acting on the particle as the particle passes from 0 to 0′ is given by

$$\overline{\mathrm{W}} = \underset{x=0}{\overline{\mathrm{E}}} - \underset{x=x}{\overline{\mathrm{E}}} = -\,k_1 \sum_{l\ (\text{even})} \sum_{j} [27] \qquad .. \quad .. \quad .. \quad (28)$$

$$= -\,k_1 \sum_{l\ (\text{even})} \sum_{j} \left[\left(\frac{x}{\sigma}\right)^l \frac{(-1)^j\ 2^{j-l+2}\ (s)\ (s+2) \ldots . (s+2j-2)}{\sigma^{s-3}\ (s+l-3)\ \underline{|2j-l+1}\ \ \underline{|l-j}} \right] \quad .. \quad (29)$$

Putting $s = (n-1)$ (see 11)

$$\overline{\mathrm{W}} = -\frac{4\,k_1}{\sigma^{n-4}} \sum_{l\ (\text{even})} \sum_{j} \left[\left(\frac{x}{\sigma}\right)^l \frac{(-1)^j\ 2^{j-l}\ (n+2j-3)\ (n+2j-5) \ldots . (n-1)}{(n+l-4)\ \ \underline{|2j-l+1}\ \ \underline{|l-j}} \right]$$

.. (30)

Now l is even, and an examination of (18) shows that as $(j+1)$ must have all the values of terms which include c^l, j will have the values,

$$\frac{l}{2},\ \frac{l}{2}+1,\ \frac{l}{2}+2,\ \cdot\ \cdot\ \cdot\ \cdot\ \cdot\ l \qquad .. \quad .. \quad .. \quad .. \quad (31)$$

It can be shown (see Appendix 1), that

$$\sum_{j} \frac{(-1)^j\ 2^{j-l}\ (n+2j-3)\ (n+2j-5) \ldots . . (n-1)}{\underline{|2j-l+1}\ \ \underline{|l-j}} \qquad .. \quad .. \quad (32)$$

where l is even and j takes the values, $\frac{l}{2},\ \frac{l}{2}+1,\ \frac{l}{2}+2, \ldots . l,$

$$= \frac{(n-2)\ (n-1) \ldots . (n+l-3)}{\underline{|l+1}} \qquad .. \quad .. \quad .. \quad .. \quad (33)$$

Hence from (30),

$$\overline{\mathrm{W}} = \frac{-4\,k_1}{\sigma^{n-4}} \sum_{l\ (\text{even})} \left(\frac{x}{\sigma}\right)^l \frac{(n-2)\ (n-1) \ldots . (n+l-3)}{(n+l-4)\ \ \underline{|l+1}} \qquad .. \quad .. \quad (34)$$

It can be shown (see Appendix 2) that

$$\sum_{\substack{l \\ (\text{even})}} \left(\frac{x}{\sigma}\right)^l \frac{(n-2)\,(n-1)\ldots.(n+l-3)}{(n+l-4)\quad \underline{|l+1}} =$$

$$\left| \frac{\left(1-\frac{x}{\sigma}\right)^{-(n-5)} - \left(1+\frac{x}{\sigma}\right)^{-(n-5)}}{2\left(\frac{x}{\sigma}\right)(n-5)\,(n-3)} + \frac{\left(1-\frac{x}{\sigma}\right)^{-(n-4)} + \left(1+\frac{x}{\sigma}\right)^{-(n-4)}}{2\,(n-4)\,(n-3)} - \frac{1}{n-4} \right|$$

.. (35)

Hence from (10), (34) and (35),

$$\overline{W} = \frac{-4\lambda N\pi}{(n-1)\,V\sigma^{n-4}} \left[\frac{X^{-(n-5)} - Y^{-(n-5)}}{2\left(\frac{x}{\sigma}\right)(n-5)\,(n-3)} + \frac{X^{-(n-4)} + Y^{-(n-4)}}{2\,(n-4)\,(n-3)} - \frac{1}{n-4} \right]$$

.. (36)

where $X = 1 - \frac{x}{\sigma}$ .. .. (37)

and $Y = 1 + \frac{x}{\sigma}$ .. .. 38)

Inserting the fundamental equation (1), (36) becomes,

$$\overline{W} = -\,4\sqrt{2}\,\pi\,\frac{\lambda\,\bar{n}}{(n-1)\,\sigma^{n-1}} \quad .. \quad .. \quad .. \quad .. \quad (39)$$

where $\bar{n}$ is put for the function in square brackets in (36).

If the effect of the attractive force be also taken into account, we can write for the total work ($\overline{W}_1$) done by the forces as the molecular centre passes from 0 to 0',

$$\overline{W}_1 = 4\sqrt{2}\,\pi\left(\frac{\mu\,\bar{m}}{(m-1)\,\sigma^{m-1}} - \frac{\lambda\,\bar{n}}{(n-1)\,\sigma^{n-1}}\right) \quad .. \quad .. \quad .. \quad (40)$$

where $\bar{m}$ corresponds to $\bar{n}$.

3. Force Equations.

The force $\overline{F}_1$ acting on the molecule along 00' is given by

$$\overline{F}_1 = \frac{d\overline{W}_1}{dx} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (41)$$

Differentiation of (39) gives

$$\frac{dW}{dx} = -\,\frac{4\sqrt{2}\,\pi\lambda}{(n-1)\,\sigma^n} \left[\frac{X^{-(n-3)} - Y^{-(n-3)}}{2\,(n-3)} + \frac{X^{-(n-4)} + Y^{-(n-4)}}{2\left(\frac{x}{\sigma}\right)(n-3)} - \frac{X^{-(n-5)} - Y^{-(n-5)}}{2\left(\frac{x^2}{\sigma^2}\right)(n-5)\,(n-3)} \right] \quad .. \quad (42)$$

and hence

$$\overline{F_1} = 4\sqrt{2}\,\pi\left(\frac{\mu\,\dot{m}}{(m-1)\,\sigma^m} - \frac{\lambda\,\dot{n}}{(n-1)\,\sigma^n}\right) \quad .. \quad .. \quad .. \quad (43)$$

where $\dot{n}$ is put for the function in square brackets in (42) and $\dot{m}$ corresponds to $\dot{n}$.

Knowing the thermal kinetic energy of a vibrating molecule, (40) enables us to calculate the displacement of a molecule from the centre of its spherical space during a vibration. It is hoped in a subsequent paper to study the application of (40) and (43) to liquids for which μ, λ, m and n have been derived from the second virial coefficient by the method of Lennard-Jones.

Summary.

Equations have been deduced for the forces on a particle vibrating in a spherical space under the influence of attractive and repulsive forces between that particle and uniformly distributed matter outside the spherical space.

The best thanks of the author are due to Professor K. R. Gunjikar, Professor of Applied Mathematics in the Royal Institute of Science, Bombay, and Professor S. D. Manerikar, Officiating Professor of Applied Mathematics in the Royal Institute of Science, Bombay, for their helpful advice in the preparation of this paper.

Appendix 1.

(With S. D. Manerikar, B.A.)

To prove that

$$\sum_j \frac{(-1)^j\,2^{j-l}\,(n+2j-3)\,(n+2j-5).....(n-1)}{\underline{|2j-l+1}\quad\underline{|l-j}}$$

where l is even and j takes the values, $\frac{l}{2}$, $\frac{l}{2}+1$,.....l,

$$= \frac{(n-2)\,(n-1).....(n+l-3)}{\underline{|l+1}} \quad .. \quad .. \quad (1)$$

Now

$$(n-3)^{-1}\,(1-z)^{-(n-3)} = \frac{1}{(n-3)} + z + \frac{(n-2)\,z^2}{\underline{|2}} + ...$$

$$+ \frac{(n-2)\,(n-1).....(n+l-3)}{\underline{|l+1}}\,z^{l+1} + ... \quad (2)$$

$$= \frac{[1 + (z^2 - 2z)]^{\frac{-(n-3)}{2}}}{(n-3)} \quad .. \quad .. \quad .. \quad (3)$$

$$= \frac{1}{(n-3)} + \frac{(-1)}{(n-3)} \cdot \frac{n-3}{2} \cdot (z^2-2z) + \frac{(-1)^2\, 2^{-2}\, (n-3)\, (n-1)\, (z^2-2z)^2}{(n-3) \quad \lfloor 2}$$

$$+ \ldots . \frac{(-1)^{j+1}\, 2^{-(j+1)}\, (n-1)\, (n+1) \ldots . (n+2j-3)\, (z^2-2z)^{j+1}}{\lfloor j+1}$$

$$+ \ldots . \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (4)$$

$$(z^2-2z)^{j+1} = z^{j+1}\, (z-2)^{j+1} \quad .. \quad .. \quad .. \quad .. \quad (5)$$

$$= z^{j+1} \left[z^{j+1} - (j+1)\, z^j \cdot 2 + \frac{(j+1)\, j}{1 \,.\, 2} z^{j-1}\, 2^2 + \ldots . \right.$$

$$\left. \frac{z^{l-j}\, 2^{2j-l+1}\, (-1)^{2j-l+1}\, (j+1)\, (j) \ldots . (l-j+1)}{\lfloor 2j-l+1} + \ldots . \right] \quad .. \quad (6)$$

The coefficient of z^{l+1} in (4) will be, therefore,

$$\sum_j \left[\frac{(-1)^{3j-l+2}\, 2^{j-l}\, (n-1)\, (n+1) \ldots . (n+2j-3)\, \lfloor j+1}{\lfloor j+1 \quad \lfloor 2j-l+1 \quad \lfloor l-j} \right] \quad .. \quad .. \quad (7)$$

where $l+1 \leqslant 2j+2$ and $\geqslant j+1$ .. .. (8)

that is, $2j+2 \geqslant l+1 \geqslant j+1$ .. .. (9)

If, however, we restrict l to even numbers, then, as j and l must both be integers, we have

$$l \geqslant j \geqslant \frac{l}{2} \quad .. \quad .. \quad .. \quad (10)$$

Hence in (7) j assumes the values,

$$\frac{l}{2}, \ \frac{l}{2} + 1, \ \frac{l}{2} + 2, \ \ldots \ldots \ l.$$

Further as l is even, $(-1)^{3j-l+2}$ in (7) can be put equal to $(-1)^j$.

The coefficients of z^{l+1} in (2) and (4) must both be equal, the coefficient in (2) is equal to the R.H.S. of (1) and the coefficient in (4) is equal to the L.H.S. of (1); hence the validity of (1) is established.

It will be noted that a similar theorem can be established for odd values of l.

Appendix 2.

To prove that,

$$\sum_{l\,(\text{even})} \left(\frac{x}{\sigma}\right)^l \frac{(n-2)\ (n-1)\ldots.(n+l-3)}{(n+l-4)\ \lfloor l+1} =$$

$$\left[\frac{\left(1-\frac{x}{\sigma}\right)^{-(n-5)}-\left(1+\frac{x}{\sigma}\right)^{-(n-5)}}{2\left(\frac{x}{\sigma}\right)(n-5)\ (n-3)}+\frac{\left(1-\frac{x}{\sigma}\right)^{-(n-4)}+\left(1+\frac{x}{\sigma}\right)^{-(n-4)}}{2\ (n-4)\ (n-3)}\right.$$

$$\left.-\frac{1}{n-4}\right] \quad .. \quad (1)$$

$$\left(1-\frac{x}{\sigma}\right)^{-(n-5)} = 1+(n-5)\frac{x}{\sigma}+\frac{(n-5)\ (n-4)}{1\ .\ 2}\left(\frac{x}{\sigma}\right)^2$$

$$+\ldots.\ \frac{(n-5)\ (n-4)\ldots.(n+l-5)}{\lfloor l+1}\left(\frac{x}{\sigma}\right)^{l+1}+\ldots. \quad .. \quad (2)$$

$$\left(1+\frac{x}{\sigma}\right)^{-(n-5)} = 1-(n-5)\frac{x}{\sigma}+\frac{(n-5)\ (n-4)}{1\ .\ 2}\left(\frac{x}{\sigma}\right)^2$$

$$+\ldots.\ \frac{(-1)^{l+1}\ (n-5)\ (n-4)\ldots.(n+l-5)}{\lfloor l+1}\left(\frac{x}{\sigma}\right)^{l+1}+\ldots. \quad .. \quad (3)$$

$(l+1)$ is odd as l is even.

Subtracting (3) from (2),

$$\frac{\left(1-\frac{x}{\sigma}\right)^{-(n-5)}-\left(1+\frac{x}{\sigma}\right)^{-(n-5)}}{2\left(\frac{x}{\sigma}\right)} = (n-5)+\frac{(n-5)\ (n-4)\ (n-3)}{\lfloor 3}\left(\frac{x}{\sigma}\right)^2$$

$$+\ldots.+\frac{(n-5)\ (n-4)\ldots.(n+l-5)}{\lfloor l+1}\left(\frac{x}{\sigma}\right)^l+\ldots. \quad .. \quad (4)$$

and,

$$\frac{\left(1-\frac{x}{\sigma}\right)^{-(n-5)}-\left(1+\frac{x}{\sigma}\right)^{-(n-5)}}{2\left(\frac{x}{\sigma}\right)(n-5)\ (n-3)}-\frac{1}{(n-3)} = \frac{n-4}{\lfloor 3}\left(\frac{x}{\sigma}\right)^2$$

$$+\frac{(n-4)\ (n-2)\ (n-1)}{\lfloor 5}\left(\frac{x}{\sigma}\right)^4$$

$$+\frac{(n-4)\ (n-2)\ (n-1)\cdot\ldots\cdot(n+l-5)}{\lfloor l+1}\left(\frac{x}{\sigma}\right)^l+\ldots. \quad .. \quad (5)$$

imilarly

$$\frac{\left(1-\frac{x}{\sigma}\right)^{-(n-4)}+\left(1+\frac{x}{\sigma}\right)^{-(n-4)}}{2\,(n-4)\,(n-3)}-\frac{1}{(n-4)\,(n-3)}=\frac{1}{\lfloor 2}\left(\frac{x}{\sigma}\right)^2+$$

$$\frac{(n-2)\,(n-1)}{\lfloor 4}\left(\frac{x}{\sigma}\right)^4+\cdots\cdot\frac{(n-2)\,(n-1)\cdots(n+l-5)}{\lfloor l}\left(\frac{x}{\sigma}\right)^l+\cdots\cdots \quad (6)$$

Hence adding (5) and (6), since

$$\frac{1}{(n-3)}+\frac{1}{(n-4)\,(n-3)}=\frac{1}{(n-4)} \quad \cdots\cdots\cdots\cdots \quad (7)$$

$$\text{R. H. S. of (1)} = \left(\frac{x}{\sigma}\right)^2\left[\frac{1}{\lfloor 2}+\frac{n-4}{\lfloor 3}\right]+\left(\frac{x}{\sigma}\right)^4\frac{(n-2)\,(n-1)}{\lfloor 4}\left[1+\frac{(n-4)}{5}\right]$$

$$+\cdots\cdot+\left(\frac{x}{\sigma}\right)^l\left[\frac{(n-2)\,(n-1)\cdots\cdot(n+l-5)}{\lfloor l}\right]\left[1+\frac{n-4}{l+1}\right]+\cdots\cdot \quad (8)$$

$$=\left(\frac{x}{\sigma}\right)^2\frac{(n-2)\,(n-1)}{(n-2)\,\lfloor 3}+\left(\frac{x}{\sigma}\right)^4\frac{(n-2)\,(n-1)\,(n)\,(n+1)}{n\,\lfloor 5}$$

$$+\cdots\cdot\left(\frac{x}{\sigma}\right)^l\frac{(n-2)\,(n-1)\ldots\ldots(n+l-5)\,(n+l-4)\,(n+l-3)}{\lfloor l+1\,(n+l-4)}+\cdots\cdot \quad (9)$$

$$= \text{L. H. S. of (1)}$$

It is interesting to note that by differentiation of both sides of (1), with regard to x we obtain, [*cf.* (42)]

$$\sum_{\substack{l\\(\text{even})}}^{l}\left(\frac{x}{\sigma}\right)^{l-1}\frac{(n-2)\,(n-1)\,\ldots\ldots\,(n+l-3)}{(n+l-4)\,\lfloor l+1}$$

$$=\frac{X^{-(n-3)}-Y^{-(n-3)}}{2\,(n-3)}+\frac{X^{-(n-4)}+Y^{-(n-4)}}{2\,\frac{x}{\sigma}(n-3)}$$

$$-\frac{X^{-(n-5)}-Y^{-(n-5)}}{2\left(\frac{x}{\sigma}\right)^2(n-5)\,(n-3)} \quad \cdots\cdots\cdots \quad (10)$$

SOME PROBLEMS OF WARING'S TYPE (III).

By Inder Chowla, B.A. (Hons.),
Lahore.

Received May 20, 1935.
(Communicated by Dr. S. Chowla.)

1. The notation used here is the same as in my previous papers[1] of the same title but is repeated for the sake of completeness. We write

$$(m)^k = (n)^k \tag{1}$$

when there exist positive integers x_s $(s \leqslant m)$, y_t $(t \leqslant n)$ such that

$$\sum_{s \leqslant m} x_s^k = \sum_{t \leqslant n} y_t^k \tag{2}$$

where

$$x_s \ (s \leqslant m) \neq y_t \ (t \leqslant n), \tag{3}$$

$$(x_1, \ldots, x_m, y_1, \ldots, y_n) = 1. \tag{4}$$

If (1) is true *infinitely often* we write

$$(m)^k = (n)^k \quad i.\ o. \tag{5}$$

$\epsilon(k)$ denotes the least possible value of $m+n$ in (5). It is trivial that $\epsilon(k) \leqslant 2k+2$. We denote by $\delta(k)$ the least value of s such that there is a constant $c = c(k)$ different from 0 such that the equation

$$c = \sum_{t=1}^{s} \epsilon_t m_t^k \quad [\text{each } \epsilon_t = 1 \text{ or } -1] \tag{6}$$

has (infinitely many) solutions in which all the m's exceed any preassigned number [$\epsilon(k)$ can also be defined as the least value of s such that (6) has infinitely many solutions with $c = o$ and $(m_1, \ldots, m_s) = 1$].

$\theta(k)$ is the least value of s such that there is a constant $c = c(k)$ such that (6) holds infinitely often with *rational* m's. Naturally

$$\theta(k) \leqslant \text{Min}\,[\delta(k), \epsilon(k)] \leqslant 2k. \tag{7}$$

Several of the results of this paper are improvements on previous ones. We show in fact that

$$(5)^6 = (6)^6 \ i.\ o. \tag{8}$$

$$\epsilon(6) \leqslant 10. \tag{9}$$

$$\delta(5) \leqslant 5. \tag{10}$$

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[1] *Proc. Ind. Acad. Sci.* (A), 1935, **1**, 694–697 and 780–781. These papers are referred to as I and II.

(11) $\theta(8) \leqslant 8.$

(12) $\theta(13) \leqslant 25.$

(13) $\text{Min } [\delta(7), \epsilon(7)] \leqslant 11.$

Remarks.—(8) was recently conjectured by Rao.[2] (9) is an improvement of the known result $\epsilon(6) \leqslant 12$ quoted in I. (10) is to be compared with Sastry's $\epsilon(5) \leqslant 6$, and it is not likely to be easily improved. (11) was announced in II [I have not yet succeeded in proving $\theta(7) \leqslant 7$]. The conjecture $\theta(k) \leqslant 2k-1$ proved here for $k=13$, seems difficult to prove for any higher value of k. (13) can also be expressed by saying that "there is an absolute constant which can be expressed *infinitely often* as a sum of 11 seventh powers of integers (positive or negative) not all having a common factor."

2. We have (as is easily verified)

(14) $$a, -a, b, -b \overset{3}{=} c, -c, d, -d$$

where

(15) $$a = \theta^2 - 2\phi^2 - 2\theta\phi, \quad b = \theta^2 - 2\phi^2 + 2\theta\phi$$

(16) $$c = \theta^2 - 2\phi^2, \quad d = \theta^2 + 2\phi^2.$$

We apply Tarry's lemma to (14) [(15), (16)] with $x=a+b$. This gives

(17) $$-b, -a, a+b+d, a+b-d, a+b+c \overset{4}{=} -c, d, -d, 2a+b, 2b+a$$

or

(18) $$a, b, 2a+2b-d, 2a+2b+d, 2a+2b+c \overset{4}{=} a+b-d, a+b+d, a+b-c, 3a+2b, 3b+2a$$

or [from (15) and (16)],

(19) $$\theta^2-2\phi^2-2\theta\phi, \theta^2-2\phi^2+2\theta\phi, 3\theta^2-10\phi^2, 5\theta^2-6\phi^2, 5\theta^2-10\phi^2 \overset{4}{=} \theta^2-6\phi^2, 3\theta^2-2\phi^2, \theta^2-2\phi^2, 5\theta^2-10\phi^2-2\theta\phi, 5\theta^2-10\phi^2+2\theta\phi$$

which we shall write as

(20) $$a_1, \ldots, a_5 \overset{4}{=} b_1, \ldots, b_5$$

[We write $a_1, \ldots, a_s \overset{k}{=} b_1, \ldots, b_s$ (A) when $\Sigma a^m = \Sigma b^m$ for $1 \leqslant m \leqslant k$. Tarry's lemma is that (A) implies

$$a_1, a_2, \ldots, b_1+x, b_2+x, \ldots \overset{k+1}{=} b_1, b_2 \ldots, a_1+x, a_2+x, \ldots]$$

Hence we have found 2 different sets of integers a_s $(s \leqslant 5)$ and b_s $(s \leqslant 5)$ such that

(21) $$\sum_{s=1}^{5} (x+a_s)^4 = \sum_{s=1}^{5} (x+b_s)^4$$

---

[2] *Jour. London Math. Soc.*, 1934, **9**, 172–173 (172).

Integrating (21) twice we get

$$\sum_{s=1}^{5}(x+a_s)^6-\sum_{s=1}^{5}(x+b_s)^6=cx+d \tag{22}$$

where (this is easily proved) $c=c(\theta,\phi)\neq 0$ except for a finite number of values of θ, ϕ. In (22) putting $x=\frac{y^6-d}{c}$ we get

$$\sum_{s=1}^{5}(y^6-d+ca_s)^6=\sum_{s=1}^{5}(y^6-d+cb_s)^6+y^6. \tag{23}$$

Since y is arbitrary (23) implies the

Theorem I. $(5)^6=(6)^6$ *i. o.*

This is (8).

3. (9) follows immediately from

Theorem II. $(5)^6=(5)^6$ *i. o.*,

which is an immediate consequence of $\theta(6)\leqslant 5$ proved in II.

4. *Proof of* $\delta(5)\leqslant 5$.

We have

$$(x+16)^5-(x-16)^5=10x^4.\,2^4+20\,.\,2^{12}.\,x^2+2\,.\,2^{20}, \tag{24}$$

$$(2x+1)^5-(2x-1)^5=10\,.\,(2x)^4+20(2x)^2.\,1^3+2\,.1^5. \tag{25}$$

Subtracting (25) from (24),

$(x+16)^5-(x-16)^5-(2x+1)^5+(2x-1)^5$

$=20\,(2^{12}-2^2)\,x^3+2\,(2^{20}-2)$.

Here putting $x=[20\,(2^{12}-2^2)]^2\,z^5$ we get

$2\,(2^{20}-2)$ expressed infinitely often as a sum of five fifth powers.

Hence $\delta(5)\leqslant 5$.

5. *Proof of* $\theta(8)\leqslant 8$.

We have

$(x+y)^8-(x-y)^8=16x^7y+112x^5y^3+112x^3y^5+16xy^7$.

Hence

$$(x+2^{12})^8-(x-2^{12})^8=2^{16}x^7+7\,.\,2^{40}x^5+7\,.\,2^{64}x^3+2^{88}x, \tag{26}$$

$$(2^6x+2^2)^8-(2^6x-x^2)^8=2^{48}x^7+7\,.\,2^{40}x^5+7\,.\,2^{32}x^3+2^{24}x. \tag{27}$$

Subtracting (27) from (26),

$$\begin{aligned}(x^8+2^{12})^8-(x^8-2^{12})^8-(2^6x^8+2^2)^8+(2^6x^8-2^2)^8\\ =(2^2x^7)^8-(2^6x^7)^8+7x^{24}\,(2^{64}-2^{32})+(2^{11}x)^8-(2^3x)^8\end{aligned} \tag{28}$$

Hence

$$7(2^{64}-2^{32}) = \left(x^5+\frac{2^{12}}{x^3}\right)^8 - \left(x^5-\frac{2^{12}}{x^3}\right)^8 - \left(2^6x^5+\frac{2^2}{x^3}\right)^8 + \left(2^6x^5-\frac{2^2}{x^3}\right)^8 - (2^2x^4)^8 + (2^6x^4)^8 - \left(\frac{2^{11}}{x^2}\right)^8 + \left(\frac{2^3}{x^2}\right)^8, \tag{29}$$

so that $\theta(8)\leqslant 8$.

6. *Proof of* $\theta(13)\leqslant 25$.

We start with Sastry's identity.[3]

$$\sum_a \{(x+a)^9+(x-a)^9\} = \sum_b \{(x+b)^9+(x-b)^9\}. \tag{30}$$

where a runs through the values 1, 7, 17, 30, 31, 36

and b runs through the values 3, 4, 19, 27, 34, 35.

Integrating (30) four times *w.r.t.* x we get

$$\sum_a \{(x+a)^{13}+(x-a)^{13}\} - \sum_b \{(x+b)^{13}+(x-b)^{13}\} = cx^3+dx, \tag{31}$$

where $c\neq 0$ (this is easily verified). Changing x into c^4y^{13} and dividing by y^{13} we get d expressed infinitely often as a sum of 25 thirteenth powers of rational numbers. Hence $\theta(13)\leqslant 25$.

7. *Proof of* Min $[\delta(7), \epsilon(7)]\leqslant 11$.

Integrating 3 times the relation (21) we get

$$\sum_{s=1}^{5}(x+a_s)^7 - \sum_{s=1}^{5}(x+b_s)^7 = cx^2+dx+e$$

where (this is easily proved) $c\neq 0$. Now

$$cx^2+dx+e = c\left(x+\frac{d}{2c}\right)^2+e-\frac{d^2}{4c}.$$

Hence putting $x+\frac{d}{2c}=c^3y$ we get $g=(2c)^7\left(e-\frac{d^2}{4c}\right)$ expressed infinitely often as a sum of 11 seventh powers of integers. We have $\delta(7)\leqslant 11$ or $\epsilon(7)\leqslant 11$ according as $g\neq 0$ or $g=0$. This, by giving θ and ϕ special values in (21) [see (19) and (20)], is merely a matter of numerical calculations.

NOTE added, June 18, 1935.—Theorem 1 [(8) above] of this paper is equivalent to the result $\gamma(6)\leqslant 6$ proved by Wright in *Journ. London Math. Soc.*, 1935, **10**, 94—99 [Theorem 2]. Wright also proves $\epsilon(8)\leqslant 15$.

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[3] In a paper recently communicated to these *Proceedings*.

LAMINAR DIFFRACTION AND THE BECKE PHENOMENON.

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

We shall concern ourselves in this paper with the optical effects arising from the passage of light through a thin plate of transparent material, the thickness or the refractive index of the substance of which exhibits more or less abrupt variations along its surface. The relation between the diffraction effects produced by such variations of thickness or refractive index and the appearance of the boundaries at which they occur when examined under the microscope is the special topic which will receive attention.

It is obvious that the effects occurring at the laminar "edges" must depend on the precise configuration of the wavefront of light after its passage through the plate. Lummer and Rieche[1] and more recently N. K. Sur,[2] who have applied the theory of microscopic vision to the case of laminar diffraction, assume that the wavefront after the passage through the plate exhibits an abrupt discontinuity on either side of the "edge". This can however be the case only if the variation in the thickness, or in the case of the variation of the refractive index the total thickness of the plate, be small compared with the wavelength of the light used. When these conditions are not satisfied, various complications will arise and the change of phase instead of being quite abrupt will be distributed over an appreciable part of the wavefront. P. N. Ghosh[3] has considered cases in which the variation in thickness takes place gradually from one point to another and has worked out the consequent diffraction effects at a distance from the plate. The influence of the shape of the laminar edge is particularly well exhibited in the case of "mixed plates," studied in detail by Prof. Raman[4] and his collaborators,

[1] Lummer and Rieche, *Bildenstehung im Mikroskop, Fr. Vieweg und Sohn* (1910), p. 75.

[2] N. K. Sur, *Proc. Ind. Ass. Cult. Sci.*, 1922, **7**, 125.

[3] P. N. Ghosh, *Proc. Ind. Ass. Cult. Sci.*, 1921, **6**, 61.

[4] Raman and Banerji, *Phil. Mag.*, 1921, **41**, 338, 860; 1921, **42**, 679; and K. Seshagiri Rao, *Proc. Ind. Ass. Cult. Sci.*, 1923, **8**, 243.

where the edges are drawn inwards under the action of surface tension and diffract a considerable amount of light through large angles in a markedly unsymmetrical manner.

N. K. Sur, as also Lummer and Rieche proceeding on the assumption of an abrupt phase change have worked out the appearance of the edge under the microscope in accurate focus. They deduce that the edge will appear as a fine dark line bordered symmetrically on either side by a set of fine equidistant fringes whose visibility quickly fades off with increasing distance from the edge. Sur himself reports, however, that his experiments show that the fringes are distinctly asymmetric in character, the visibility and the number being greater on the retarded side than on the other. This asymmetry becomes more pronounced as the microscope is put out of focus.

2. The Becke Phenomenon.

When a low-power microscope is focussed on a laminar "edge" the latter is seen in focus as a dark line. As the microscope is gradually disturbed from the focus a bright line detaches itself from the dark line and moves laterally : it moves towards the retarded side as the microscope is raised from its position of focus and moves towards the other side when the microscope is lowered. These effects constitute what is known the Becke Phenomenon, the bright line being referred to as the "Becke line". When the line is caused by a variation in thickness it may be used to determine the refractive index of the specimen. Liquids of known different refractive indices are tried as films on the plate till the "Becke line" vanishes. This happens when the refractive indices of the specimen and the liquid agree completely.

The usual explanation of the Becke phenomenon is based on geometrical optics. When a convergent beam of light is used to illuminate the specimen, some of the rays striking the "edge" from the side of the greater refractive index will undergo total internal reflection. Therefore over a narrow region on the retarded side there will be more rays entering the microscope than on

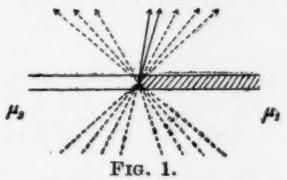

FIG. 1.

the other side. When the microscope is focussed at the edge itself the light will be brought to a point conjugate with the edge itself. But when raised from that position the microscope is really focussed on a plane above the plate and the excess of light, resulting from total internal reflection, is

focussed to a point in the image plane conjugate to a point *near* the "edge". Its distance from the edge increases as the distance of the "focussed" plane from the specimen increases.

This explanation demands the disappearance of the phenomenon in parallel light incident normally to the plate. But the phenomenon is found to persist here as well. It seems, therefore, that the simple geometrical explanation is inadequate. In what follows an attempt is made to explain the asymmetry observed both in and out of focus as diffraction effects produced by the edge, by adopting a certain modification in the form of the emerging wavefront, as suggested by Prof. Raman[5] in a recent paper.

3. The Theory.

We consider plane waves incident normally on the specimen. Denoting by 2ρ the excess of path retardation suffered by one half of the wave over the other in its passage through the plate, we have

$$2\rho = (\mu_1 - \mu_2)\, t$$

where μ_1 is the greater refractive index, μ_2 the other refractive index and t the thickness. As mentioned before, N. K. Sur assumes that the wavefront after its passage through the plate exhibits an abrupt discontinuity on either side of the edge (Fig. 2). This can hold good only when the thickness is very small. With a greater thickness comparable with the wavelength of light, it is not likely that the discontinuity of the wavefront will be so sharp; the discontinuity will extend over a range and may be tentatively taken to have a straight slope from $-X_1$ to $+X_1$ (Fig. 3).

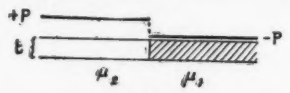

FIG. 2.

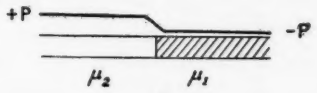

FIG. 3.

Now the phase of the wavefront as it emerges from the specimen will be represented by

$$+\rho \quad \text{from } X = -\infty \text{ to } -\frac{\rho}{k},$$

$$-kX \quad \text{from } X = -\frac{\rho}{k} \text{ to } +\frac{\rho}{k}$$

and

$$-\rho \quad \text{from } X = \frac{\rho}{k} \text{ to } +\infty.$$

$-k$ represents the slope of the wavefront at the "edge".

The expression[6] for the resultant amplitude of light wave at a point in

[5] Sir C. V. Raman, *Proc. Ind. Acad. Sci.*, 1935, 1, 585.

[6] Lummer Rieche, *Loc. cit.*, p. 90.

the image plane of the microscope conjugate to a point (x, y) in the object plane due to a luminous point (X,Y) in the object plane is given by

$$S = \frac{k}{\lambda^2} \iint_{\text{Aperture}} d\xi \, d\eta \iint_{\text{Object}} \phi(X, Y) \cdot \sin \frac{2\pi}{\lambda} \{Vt-(x-X)\,\xi-(y-Y)\,\eta + \psi(X, Y)\}\, dX.\, dY.$$

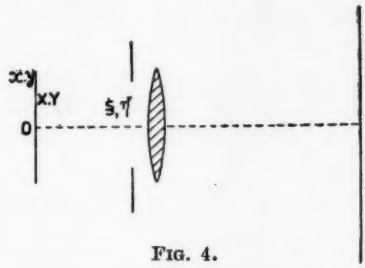

FIG. 4.

ξ, η are the angular co-ordinates of a point in the aperture with respect to O, ϕ (X, Y) is the transmission coefficient at the point (X, Y), and ψ (X, Y) the corresponding phase.

When we consider an object and a rectangular aperture both symmetric with respect to the Y axis, the expression reduces to

$$S = \frac{e}{\lambda} \int_{\text{Object}} dX \int_{-\xi}^{+\xi} \phi(X) \cdot \sin \frac{2\pi}{\lambda} \{Vt-(x-X)\,\xi+\psi(X)\}\, d\xi$$

We may take the transmission coefficient to be the same for both the media, so that ϕ (X) is a constant. The factor $\frac{2\pi}{\lambda}$ may be omitted for convenience only to be restored for numerical calculations. The variation of the phase ψ (X) over the wavefront has already been given. Then, omitting constants,

$$S = \int_{-\infty}^{-\frac{\rho}{k}} dX \int_{-\xi}^{+\xi} \sin \{Vt-(x-X)\,\xi+\rho\}\, d\xi$$

$$+ \int_{-\frac{\rho}{k}}^{+\frac{\rho}{k}} dX \int_{-\xi}^{+\xi} \sin \{Vt-(x-X)\,\xi-kX\}\, d\xi$$

$$+ \int_{\frac{\rho}{k}}^{\infty} dX \int_{-\xi}^{+\xi} \sin \{Vt-(x-X)\,\xi-\rho\}\, d\xi.$$

If we represent

$$\int_0^x \frac{\sin x}{x}\,dx \text{ by Si } (x), \text{ and } \int_\infty^x \frac{\cos x}{x}\,dx \text{ by Ci } (x)$$

we have

$$S = \sin Vt \cdot \cos \rho \left[\pi - \text{Si}\left(x+\frac{\rho}{k}\right)\xi + \text{Si}\left(x-\frac{\rho}{k}\right)\xi\right] + A \sin Vt$$

$$+ \cos Vt \cdot \sin \rho \left[\text{Si}\left(x+\frac{\rho}{k}\right)\xi - \text{Si}\left(x-\frac{\rho}{k}\right)\xi\right] - B \cos Vt,$$

$$\text{where} \quad A = \int_{-\frac{\rho}{k}}^{+\frac{\rho}{k}} \frac{\sin (x-X)\,\xi}{(x-X)\,\xi} \cdot \cos (kX)\,dX,$$

$$\text{and} \quad B = \int_{-\frac{\rho}{k}}^{+\frac{\rho}{k}} \frac{\sin (x-X)\,\xi}{(x-X)\,\xi} \sin (kX)\,dX.$$

When integrated

$$A = \text{Si}\,(k+\xi)\left(x+\frac{\rho}{k}\right) - \text{Si}\,(k+\xi)\left(x-\frac{\rho}{k}\right)$$

$$+ \text{Si}\,(k-\xi)\left(x+\frac{\rho}{k}\right) - \text{Si}\,(k-\xi)\left(x-\frac{\rho}{k}\right)$$

and

$$B = -\text{Ci}\,(k+\xi)\left(x+\frac{\rho}{k}\right) + \text{Ci}\,(k+\xi)\left(x-\frac{\rho}{k}\right)$$

$$+ \text{Ci}\,(k-\xi)\left(x+\frac{\rho}{k}\right) - \text{Ci}\,(k-\xi)\left(x-\frac{\rho}{k}\right).$$

The intensity is given by the sum of the squares of the coefficients of $\sin Vt$ and $\cos Vt$ in the expression for S. The intensity curves are drawn for different values of the path retardation 2ρ, using different values for k, with the help of tables for Ci and Si functions computed by Glaisher.[7]

In the calculations the value of ξ the semiangular aperture of the objective of the microscope is taken as 0·5. The abscissa of the curves are values of $\frac{2\pi}{\lambda} x\xi$.

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[7] G. W. L. Glaisher, *Phil. Trans. Roy. Soc.* A, 1870, p. 367.

Slope $k = 1$.

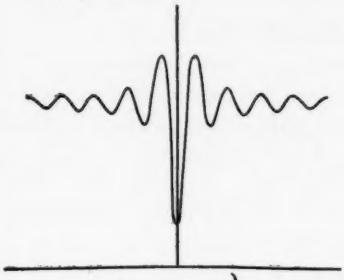

FIG. 5. $2\rho = \frac{\lambda}{3}$.

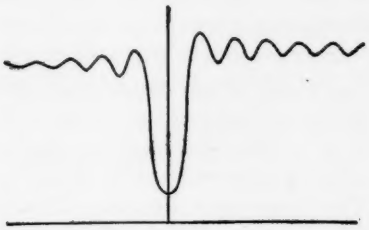

FIG. 6. $2\rho = 2\frac{1}{3}\lambda$.

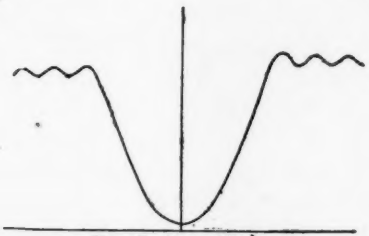

FIG. 7. $2\rho = 6\frac{1}{3}\lambda$.

Fig. 5 is drawn for the value of $2\rho = \frac{\lambda}{3}$, a fraction of a wavelength. It shows no asymmetry. The maxima and minima are sharp and equispaced. Fig. 6 is drawn for the value of $2\rho = 2\frac{1}{3}\lambda$, of the order of a few wavelengths. It shows some asymmetry on the right side. But the minimum at the edge is smaller than in the previous case and is distinctly wider. Fig. 7 represents the illumination when 2ρ is much greater. The central minimum widens out considerably.

Slope $k = \frac{1}{4}$.—The slope is small enough to allow the majority of the diffracted rays into the microscope.

FIG. 8. $2\rho = \frac{\lambda}{3}$.

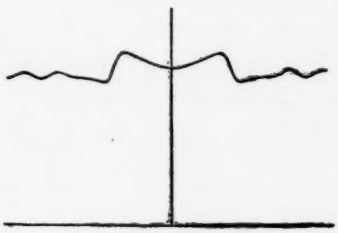

FIG. 9. $2\rho = 2\frac{1}{3}\lambda$.

Fig. 8 is drawn for the value of $2\rho = \frac{\lambda}{3}$, a fraction of a wavelength. The fringes are asymmetric with a sharp central minimum. But as the retardation increases the extent of the sloped part of the wavefront increases and the fringes are practically washed out. Fig. 9 is drawn for the value of $2\rho = 2\frac{1}{3}\lambda$.

P. N. Ghosh[8] has worked out the Fresnel diffraction pattern, caused by a wavefront of the form we have postulated, at a large distance in front of it. When we consider a pattern close to the edge, only the size of the pattern is diminished, so that it is not necessary to work out the details here. The microscope when out of focus with respect to the laminar edge is really focussed on this Fresnel pattern. The general form of the pattern is as reproduced below.

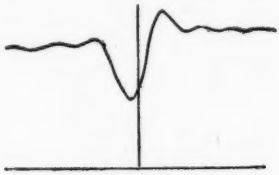

FIG. 10.

This explains why the asymmetry becomes prominent as the microscope is put out of focus. It merely magnifies the Fresnel diffraction pattern produced by the deformed wavefront.

The form of the wavefront postulated evidently succeeds in accounting for a certain amount of asymmetry in the pattern observed in a microscope in accurate focus. It also accounts for the asymmetry of the pattern when the microscope is put out of focus. A rigorous solution of the problem is, however, desirable which takes into consideration the boundary conditions at the two surfaces and also at the "edge" of the transparent medium. The treatment given by Raman and Rao[9] on the lines of Sommerfeld's solution of the problem of diffraction by a straight edge explains the existence of large angle diffraction by the laminar boundary but not the asymmetry considered in the present paper.

4. Visibility of Laminar Boundary.

It is interesting to calculate the minimum path retardation that may be detected by the observation of a dark line in the microscope under direct illumination. Following Michelson let us call the expression

$$\frac{I_{max} - I_{min}}{I_{max} + I_{min}}$$

[8] P. N. Ghosh, *Proc. Ind. Ass. Cult. Sci.*, 1921, **6**, 61.
[9] Raman and Rao, *Proc. Phy. Soc.*, 1927, **39**, 453.

the visibility of the fringe system. In the present case

$$I_{max} = \pi \cos \rho + \left(\frac{\pi}{2} + 0{\cdot}28\right).2 \sin \rho.$$

and

$$I_{min} = \pi \cos \rho.$$

According to the criterion of visibility due to Lord Rayleigh, the fringe system will cease to be visible when its visibility as defined before, comes down to $\frac{1}{40}$. Solving for ρ, we get in the limiting case

$$\rho = 2\tfrac{1}{2}^\circ \text{ (approximately)}$$

i.e., $2\rho = 5^\circ$ or corresponds to a retardation of $\frac{\lambda}{72}$.

This gives a lower limit to the detectable path retardation when viewed in direct light. When, however, the edge is viewed in oblique illumination and appears as a bright line, its visibility will be limited only by the background illumination if any, and much smaller changes of thickness should be visible, provided they are sufficiently abrupt.

Let me record here my humble thanks to Sir C. V. Raman, Kt., F.R.S., N.L., for the suggestion of the problem and the keen interest he took in the work.

5. *Summary.*

A sharp laminar edge appears as a dark line bordered by asymmetric fringes when examined in direct illumination under a microscope. The theories of Lummer and Rieche as also Sur, based on the assumption of an abrupt change of phase in the emerging wavefront, fail to account for this asymmetry. The Becke phenomenon—the appearance of a bright line close to the dark line corresponding to the " edge " when the microscope is put out of focus—merely represents the strongly asymmetric character of the pattern in the out-of-focus position as well. The simple geometrical explanation of the phenomenon as usually given is shown to be inadequate as it fails with normal parallel light. It is postulated that the phase change caused by the edge is not abrupt but is gradual and extends over a part of the emerging wavefront. The theory of microscopic vision as applied to such a deformed wavefront shows the pattern as observed in focus to be asymmetric. The same postulate also explains the asymmetry in the out-of-focus position—the Becke Phenomenon. Thus the asymmetric microscopic appearances both in and out-of-focus are explained as due to asymmetric diffraction effects at the edge. An estimate of the smallest path retardation that may be detected under direct illumination is also made.

POTENTIAL DISTRIBUTION IN INFINITE CONDUCTORS AND UPLIFT PRESSURE ON DAMS.

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When a dam is built on porous strata such as generally exist at the beds of rivers, there is an underground flow through the porous strata under the masonry, from the upstream to the downstream. Accompanying this flow there will be a pressure acting upwards from below on the masonry floor. An accurate knowledge of this uplift pressure and the nature of its distribution is of fundamental importance for purposes of designing a dam. There have been many attempts to investigate by direct measurements from laboratory models of dams, the way in which this pressure varies with different forms of design. The usual method for model work is to build a tank of convenient size with a number of holes fitted with manometers. The tank is then filled with sand representing the sub-soil strata and the model of the dam is placed on the sand. A head of water is maintained on the upstream side of the model of the dam and the pressure distribution is indicated by the manometers. A very large number of measurements and readings are required to obtain satisfactory results. The above method is very laborious.

An accurate and quick method for studying this pressure distribution was therefore highly desirable. From the analogy between the Ohm's law for conduction of electricity and Darcy's law for the conduction of water through porous media, N. N. Pavlovsky[1] suggested as early as 1921, that an electrical method could be employed, for the purpose of studying the sub-soil pressures under dams. Some attempts were made in this direction by Lane and co-workers[2] in America, but no definite conclusion was arrived at. The experimental evidence was very unconvincing and the electrical method stood almost rejected. The question whether the electrical method gave results agreeing with direct measurements or not, is of fundamental importance. For if the potential distribution in conductors is the same as the pressure distribution in the sub-soil under the models of dams, then the potential law and the equations of Laplace can be employed for the study of this pressure distribution. If the Laplace equations do apply, then the

mathematical foundation for the flow of water under dams is established. If the Potential law does not hold then the problem of sub-soil flow under dams must be attacked from a different standpoint. It was therefore highly desirable to investigate the problem very accurately and compare the results obtained by different methods, theoretical as well as experimental.

In investigating the various cases we were limited to two simple types (1) A simple impervious floor flush with the surface of the porous strata, (2) The same case with sheet-piles.* For both cases, theoretical solutions and direct measurements in models existed and so the results of the electrical method could be compared with direct observation of pressure and with theoretical solutions.

2. *Experimental.*

The apparatus for the electrical experiment consists of two parts, the model tank and the source of the alternating current. These are shown in Fig. 1. The tank is 4 feet long and 3 inches deep. AB and CD are two thick conducting plates of copper each 1·5 feet long representing the surfaces of the porous strata on the upstream and downstream of the dam. BC is an ebonite plate 1 foot long and flush with the conductors representing the non-porous masonry of the dam.

In the first set of experiments the tank was rectangular being about $4' \times 3' \times 3''$. It was thought that the potential distribution round BC would not be affected by the outer boundary, but it was found that this introduced an error of about 5 per cent. The outer boundary ARD of the tank was then made elliptical in shape with B and C as foci. The elliptical shape of the boundary conforms to the theoretical condition, that the boundary is at an infinite distance away. The tank S is filled with a dilute solution of ammonium chloride. P is a probe made by fusing a platinum wire into a glass tube, the end of the wire alone being exposed. P_1 is a jockey moving on a ten-metre potentiometer wire WW_1. T is a headphone connected as shown in the figure.

The potentiometer wire serves as a potential divider. The ends of the potentiometer are connected in parallel with the A.C. source and with the conducting plates as is shown in the diagram (Fig. 1). The wire was accurately calibrated.

The A.C. source (Fig. 1) is obtained from a Neon oscillator with an amplifier. This arrangement which is shown completely in Fig. 1 is a very convenient source of oscillating current and a sharp null point is obtained in

* A sheet-pile is an impervious obstruction driven generally at right angles to the impervious horizontal floor into the sub-soil.

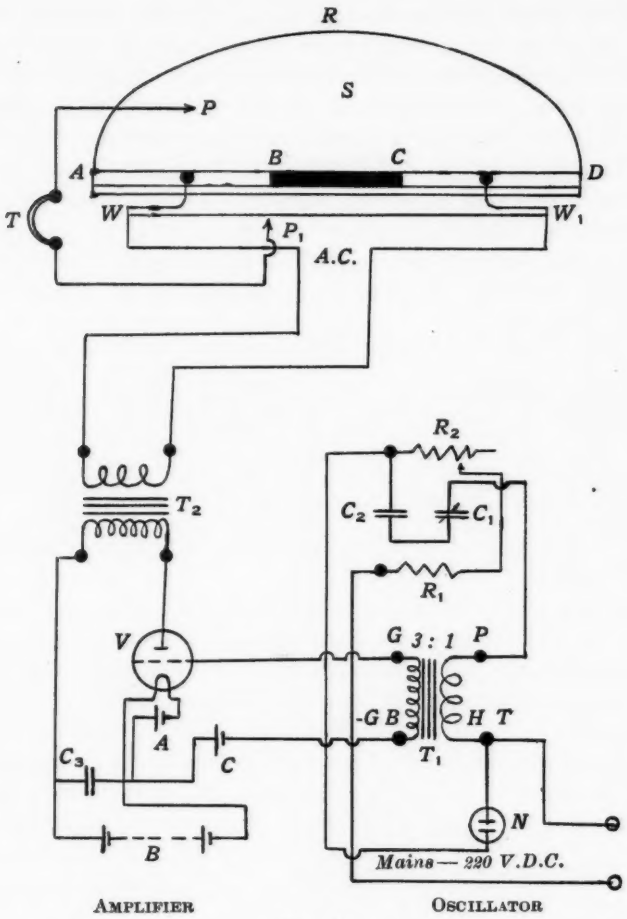

FIG. 1.

C_3—Fixed Condenser	N —Neon Bulb
V —Triode Valve	R_1—High Resistance
T_2—Transformer	R_2—Rheostat
A —Filament Battery	C_1—Variable Condenser
B —Plate Battery	C_2—Fixed Condenser
C —Grid Battery	T_1—Transformer

the phone. A high accuracy in determining the null point is required in this experiment, because it can be seen from the arrangement that the total fall of potential between the ends of BC is equal to the fall at the ends of ten metres in the potentiometer and the problem is to determine very

accurately the potential of the various points along BC. The present arrangement for determining the potential was found so good that the null points in the phone could be determined with absolute certainty. The success of the experiment was mainly due to this part of the technique. The method may be employed with advantage for measurement of resistances where an A.C. is to be used.

In the preliminary experiments where ordinary buzzers were used, no definite results were obtained.

The details of the arrangement can be understood from the diagrammatic sketch in Fig. 1.

3. *Method of Observation.*

In carrying out an experiment, the moving contact P_1 in the potentiometer (Fig. 1) is placed at 1/20th of the potential and by probing with the help of P, the series of null points corresponding to this potential are marked in the tank. P_1 is then moved to 2/20th of the potential and the observations are then repeated. A complete set of equipotential lines for decrements of 5 per cent. of the total potential drop is thus traced on the bottom of the tank. To facilitate the direct marking of the points, the bottom of the tank was made of ground glass. Tracings of the points are then made and reduced to a convenient size for comparison.

4. *Direct Measurements.*

As pointed out in the introduction, the direct measurements on model were carried out in tanks.

The size of the tank for direct measurements was the same as for the electrical method, to facilitate comparison. The details of the method for direct measurement of pressures under models are given in a memoir of the Institute.[3]

5. *Theoretical Calculations.*

The theoretical calculations for the distribution of pressures mentioned in cases 1 and 2 have been made by Weaver.[4] In the case of the simple impervious floor the solution for the pressure lines gives a confocal system of hyperbolæ with the end of the masonry as foci. This corresponds to the system of equipotential lines obtained in the case of a magnetic or electric dipole in an analogous case. The lines of force are a system of ellipses with the poles as foci, *i.e.*, in the case of flow of water the streamlines would correspond to a similar system of ellipses. In obtaining the solution, the potential law of flow was assumed. In the simple case mentioned, the solution for the pressure distribution will be an *S* curve. When a sheet-pile is introduced at one end, the system of equipotential or equipressure lines becomes very complicated and the mathematical solution difficult.

Weaver[4] has worked out a theoretical solution for the case of one sheet-pile and reference may be made to that paper for details of the calculations. For the sake of clearness, one diagram from his paper giving a graphical representation of the mathematical calculation is reproduced in Fig. 2. For ordinary cases of weirs which are generally very complicated, the mathematical solutions have not yet been obtained and they are very difficult. Only experimental solutions for the pressure distribution for the complicated cases are thus possible.

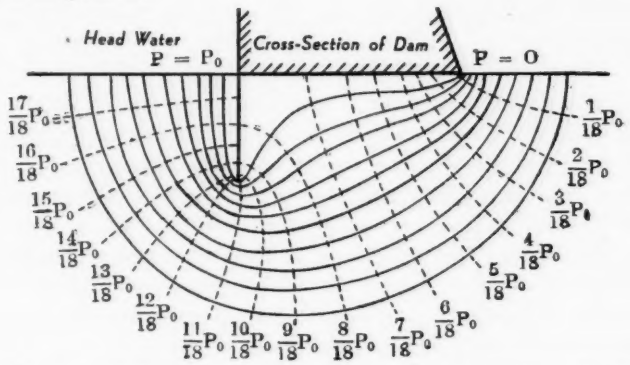

FIG. 2. Lines of Seepage Flow and Lines of Equal Pressure under Dam with Sheet-Piling.

(*Reproduced from the Journal of Mathematics and Physics, June 1932.*)

6. *Results.*

The results are represented graphically in Figs. 3 and 4.

CASE I.

A simple impervious floor flush with the surface of the porous strata.—The complete system of potential lines obtained from the electrical method, direct measurements and theoretical calculations are shown in Fig. 3, only one half of the system being shown. The difference between the results of the electrical method and that of theoretical calculations was generally less than 0·2%. This small error was due to resistances at the contacts and of the leads. The difference between the results of the direct measurements and those of the electrical method was about 3%. This agreement should be taken as remarkably good when the various sources of error and difficulties of measurements in the direct method are considered.

The potential distribution on the non-conductor corresponding to the pressure distribution along the bottom of the masonry is compared in Curve 1, Fig. 4. The points obtained by the two methods and those of the theoretical

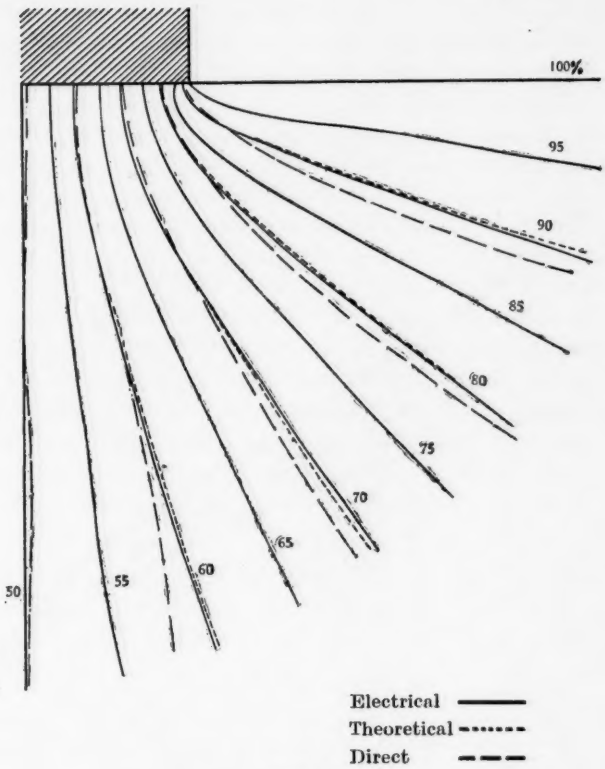

FIG. 3.
Flush Case of the Floor.

calculations fall on the curve showing that the results of the electrical method are identical with those of direct measurements and of theoretical calculations.

In the curves α represents the ratio of the length of the horizontal masonry to that of the sheet-pile. $\alpha = \infty$ therefore means that there is no sheet-pile.

CASE II.

(*a*) *Same as Case* (*I*) *with a sheet-pile at an end.*—When a non-conductor of 2·4 inches is introduced at one end, at right angles to the non-conductor which is twelve inches long, the ratio α becomes 5. The results of the electrical method, of direct measurements and of the theoretical calculations for such a case are compared in Curve 2, Fig. 4. The pressure distribution along the horizontal part is alone shown in the diagram. The results again agree.

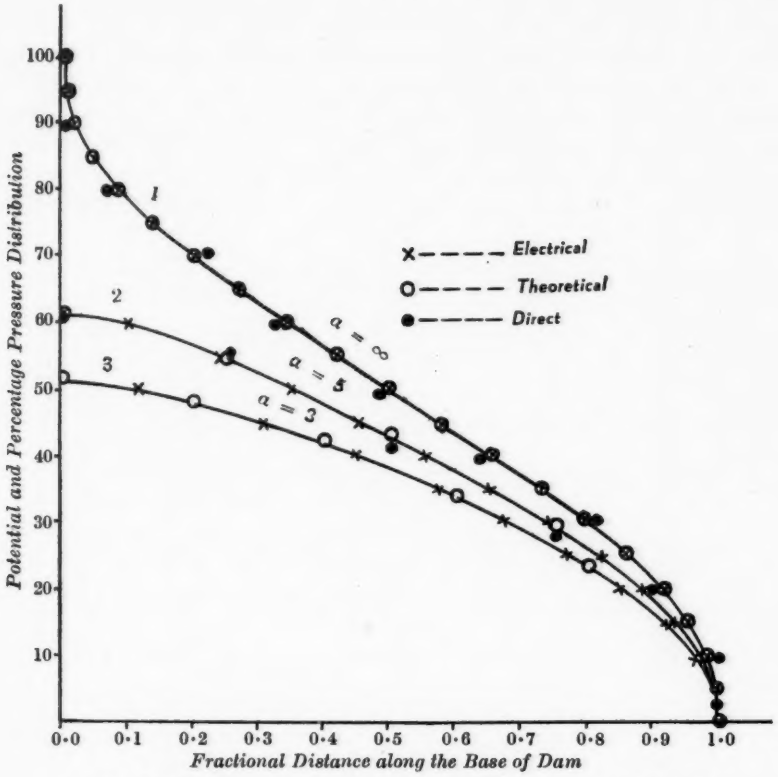

FIG. 4. Distribution of uplift pressure across Base of Dam in per cent. of headwater pressure for various Ratios and of width of Base of Dam to depth of Sheet-Piling at the Heel.

(*b*) *A simple floor with a sheet-pile the ratio* a *being* 3.—In this case no direct measurements were available. The results obtained by the electrical method again agree with those of the theoretical calculations as shown in Curve 3, Fig. 4.

OTHER CASES.

Some other cases of complicated models were also examined by the electrical method and the results were compared with those from direct measurements. The results in those cases agreed, but they are of more practical importance to the engineers, and no mathematical calculations have so far been made for them. They are not therefore shown here.

7. *Discussion.*

It is obvious from the results obtained that *the law of flow of water in the sub-soil under dams is the same as the law of potentials in conductors.* That previous experimenters failed to obtain identical results from direct measurements and from the electrical method, must be attributed to faulty technique in their methods. The fact that the potential distribution in conductors and the pressure distribution in the sub-soil under dams are of the same form, establishes the mathematical foundation for designs of such works and as such should be considered as a great advance on our existing knowledge. The experiments also incidentally verify the theory worked out by Weaver. From the practical standpoint, it becomes very easy now by the electrical method to determine the pressure distribution for any complicated design of a dam. It is however worth while to remark that the geological conditions such as stratification of the layers modify the pressure distribution, but this is a local condition and does not alter the fundamental basis of the laws of design. Attempts are being made in the Institute to try to simulate the geological conditions as well.

Summary.

It has been shown by experiments that the distribution of pressure in the sub-soil under dams is the same as potential distribution in conductors. The theoretical basis of sub-soil pressures under dams is thus established.

REFERENCES.

1. Reference to Pavlovsky's work is found in the *Proceedings of the International Congress of Dams,* 1933.

2. Lane and others.—*Technical Memorandum,* 1934, Nos. 384 and 388. United States Department of the Interior Bureau of Reclamation.

3. E. M. Taylor and H. L. Uppal.—*Research Publication of the Punjab Irrigation Research Institute,* February 1934, 2, No. 6.

4. Warren Weaver.—*Journal of Mathematics and Physics,* 1932, 11, No. 2, 114. Refer also to Lamb's *Hydrodynamics,* page 70, 4th Edition.

THE NEAR ULTRA-VIOLET ABSORPTION BANDS OF SO_2.

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The absorption bands of SO_2 have been measured and the number of recorded bands considerably increased. The analysis of this band system is still to a large extent arbitrary and several arrangements of the bands are possible. Since, however, the symmetric valence vibration of unexcited SO_2, as known from Raman Effect and infra-red spectrum, has nearly the same value as the vibration of the molecule SO, known from its band spectrum, preference is given to an arrangement of the SO_2 bands, by which the symmetric valence vibration of excited SO_2 gains almost exactly the same values as that of excited SO.

The absorption bands of sulphur dioxide in the near ultra-violet have been studied in more recent years by several authors. Dutta[1] obtained a small number of the bands whereas Watson and Parker[2] reported a large number of them. Dutta's analysis covers only a limited number of bands even among the bands obtained by him, whereas that of Watson and Parker is open to serious objections as pointed out by Dutta and later workers. The most serious is certainly that they obtain three different origins which is obviously impossible. Clements[3] has given a new analysis of the bands recently. He has chosen a rather weak band at 31945 cm.$^{-1}$ as the $(0, 0, 0)'' \rightarrow (0, 0, 0)'$ transition on account of its behaviour under different temperatures. It should be possible indeed to single out the $(0, 0, 0)'' \rightarrow (0, 0, 0)'$ band on these considerations of changes in intensity with temperature. But the particular procedure adopted by him contains a number of theoretical and experimental simplifications and therefore 31945 cm.$^{-1}$ is not the only possible value for this transition. We have shown in this paper that the subsidiary maxima which accompany the main ones are also independent bands. Therefore intensity measurements become even more difficult because such subsidiary maxima can arise in quite different ways, *e.g.*, by a complete overlap of a strong broad band and a weak one or by the partial overlap of two narrow bands of about equal intensity. Clements has divided the bands into two different groups—the low frequency group and the high frequency group. The high frequency group consists of composite transitions to the vibrational levels of two modes of vibrations in the excited state of the molecule from the vibrationless state of the ground level, while the low frequency group arises

from transitions from the vibrational levels of the excited state of the ground frequency 525 to various vibrational levels of the normal state of the molecule. This division of the bands into two distinct groups means physically that the excited vibrational levels of the ground term of the two modes 525 and 1144, which are used for thee xplanation of the low frequency bands, do not combine with the excited vibrational levels of the excited terms of the 1144 mode, which are used for the explanation of the high frequency bands. Theoretically a selection rule which forbids such transitions is of course not known. We have observed the bands during our study[4] of the absorption of the chlorides and oxychlorides of sulphur under different conditions. We rather think it likely that all the bands are more intimately connected with one another. To our mind there are also some other reasons which go against the analysis proposed by Clements. Firstly, according to the Franck-Condon diagram, we would not expect the band at the origin to be just one of the weakest, unless of course there is an abnormal change in internuclear distances on excitation. Secondly, he obtains in the excited state of the molecule, the frequency of symmetric deforming vibration decreased while that of the symmetric valence vibration increased. On the other hand, we have found a possibility of a different analysis which has a certain advantage. It is well known from infra-red and Raman spectra[5] that in SO_2 the symmetric valence vibration has about the same value as that of SO in the ground state, which again agrees with the fact that the energy of the S=O band remains very nearly constant.[4] In the analysis proposed here, also the symmetric valence vibration in the excited state of SO_2 is of the same order of magnitude as that of the excited state of SO. At the same time our analysis interprets the bands as a uniform system, *i.e.*, those on the high frequency side as due to transitions from the lower vibration levels of the ground state and those on the low frequency side as transitions from higher vibrational levels of the ground state.

Experimental.

The bands were obtained in the usual way with the apparatus described elsewhere[4] at different temperatures and pressures. Spectrograms were taken with pure SO_2 and with SO_2 in the presence of other vapours like SCl_2, $SOCl_2$, etc. The plates were run on the recording microphotometer with different enlargements. The microphotograms were then measured by an Abbe comparator, and thus the bands as well as the standard lines which were also present on the microphotogram were directly compared. Several microphotograms were measured and the wave-lengths of the bands calculated by the usual Hartmann dispersion formula agreed to 0·3 A.U. The mean value of the wave-lengths was then taken so that the accuracy obtained was within

5 to 7 cm.$^{-1}$ This allowed us to include also such bands which appear as subsidiary maxima due to overlapping. Only such subsidiary maxima, as were common to all the plates measured, have been included. On the still shorter wave-length side where the bands become diffuse, it was not possible to identify with certainty more bands than are tabulated here. Clements, however, has measured a few additional bands in this region which probably can be included in the present analysis within the error of his measurements. Table I gives the list of bands and Fig. 1 (Plate I) is a sample photometer curve. The lower frequency bands have not been measured but the values given by Clements are utilised for the time being to show that it is possible to extend the present analysis to them.

TABLE I.

λ (A.U.) in air	ν vac	Classification
3131·3	31926 A_1	$(0, 1, 2)'' \rightarrow (0, 1, 2)'$
3130·3	31937 A_2	$(0, 0, 2)'' \rightarrow (0, 2, 0)'$
3107·8	32168 B	$(0, 1, 0)'' \rightarrow (0, 0, 0)'$
3087·6	32378 C_1	$(0, 2, 0)'' \rightarrow (0, 2, 0)'$
3086·2	32393 C_2	$(0, 0, 2)'' \rightarrow (0, 0, 2)'$
3067·9	32586 D_1	$(0, 1, 2)'' \rightarrow (0, 2, 2)'$
3066·0	32606 D_2	$(0, 0, 2)'' \rightarrow (0, 3, 0)'$
3046·3	32817 E_1	$(0, 0, 1)'' \rightarrow (0, 0, 1)'$
3044·6	32836 E_2	$(0, 1, 0)'' \rightarrow (0, 1, 0)'$
3043·8	32844 E_3	$(0, 2, 0)'' \rightarrow (0, 0, 2)'$
3025·0	33048 F_1	$(0, 2, 0)'' \rightarrow (0, 3, 0)'$
3023·4	33066 F_2	$(0, 0, 2)'' \rightarrow (0, 1, 2)'$
3005·8	33259 G_1	$(0, 0, 2)'' \rightarrow (0, 4, 0)'$
3001·9	33303 G_2	$(0, 0, 0)'' \rightarrow (0, 0, 0)'$
2985·4	33487 H	$(0, 1, 0)'' \rightarrow (0, 2, 0)'$ or $(0, 0, 1)'' \rightarrow (0, 1, 1)'$

λ (A.U.) in air	ν vac	Classification
2966·5	33700 I_1	$(0, 2, 0)'' \rightarrow (0, 4, 0)'$ or $(0, 0, 2)'' \rightarrow (0, 2, 2)'$
2964·8	33719 I_2	$(0, 0, 1)'' \rightarrow (0, 0, 2)'$
2962·7	33743 I_3	$(0, 2, 0)'' \rightarrow (0, 0, 3)'$ or $(0, 1, 0)'' \rightarrow (0, 1, 1)'$
2946·6	33928 K_1	$(0, 0, 1)'' \rightarrow (0, 3, 0)'$
2944·9	33947 K_2	$(0, 1, 0)'' \rightarrow (0, 0, 2)'$
2943·7	33961 K_3	$(0, 0, 0)'' \rightarrow (0, 1, 0)'$
2926·8	34157 L_1	$(0, 1, 0)'' \rightarrow (0, 3, 0)'$
2924·4	34185 L_2	$(0, 0, 0)'' \rightarrow (0, 0, 1)'$
2908·8	34368 M	$(0, 0, 2)'' \rightarrow (0, 3, 2)'$
2889·1	34603 N_1	$(0, 0, 1)'' \rightarrow (0, 0, 3)'$
2888·3	34612 N_2	$(0, 0, 0)'' \rightarrow (0, 2, 0)'$
2869·0	34845 O	$(0, 1, 0)'' \rightarrow (0, 0, 3)'$ or $(0, 0, 0)'' \rightarrow (0, 1, 1)'$
2853·7	35047 P_1	$(0, 0, 2)'' \rightarrow (0, 4, 2)'$
2850·0	35078 P_2	$(0, 0, 0)'' \rightarrow (0, 0, 2)'$
2833·3	35284 Q	$(0, 0, 0)'' \rightarrow (0, 3, 0)'$
2819·1	35462 R_1	$(0, 0, 2)'' \rightarrow (0, 2, 4)'$
2817·5	35482 R_2	$(0, 2, 0)'' \rightarrow (0, 4, 2)'$
2800·3	35700 S	$(0, 1, 0)'' \rightarrow (0, 0, 4)'$
2781·0	35948 T_1	$(0, 0, 0)'' \rightarrow (0, 4, 0)'$
2779·3	35970 T_2	$(0, 0, 0)'' \rightarrow (0, 0, 3)'$
2766·3	36139 U	$(0, 0, 2)'' \rightarrow (0, 3, 4)'$
2747·3	36389 V	$(0, 0, 0)'' \rightarrow (0, 2, 2)'$
2681·1	37287 W	$(0, 0, 0)'' \rightarrow (0, 2, 3)'$

TABLE II.

	(0, 0, 0)″		(0, 1, 0)″		(0, 2, 0)″
(0, 0, 0)′	31937 A_2 458	1136	(30801) 440	1109	(29692) 447
(0, 1, 0)′	32393 C_2 451	1152	(31241) 478	1102	(30139) 443
(0, 2, 0)′	32844 E_3 459	1125	(31719) 449	1137	(30582) 446
(0, 3, 0)′	33303 G_2 440	1135	32168 B 438	1140	(31028)
(0, 4, 0)′	33743 I_3 442	1137	32606 D_2 460		—
(0, 5, 0)′	34185 L_2 427	1119	33066 F_2 421	1140	31926 A_1 452
(0, 6, 0)′	34612 N_2 466	1125	33487 H 441	1109	32378 C_1 458
(0, 7, 0)′	35078 P_2 404	1150	33928 K_1 440	1092	32836 E_2 423
(0, 8, 0)′	35482 R_2 466	1114	34368 M 477	1109	33259 G_1 460
(0, 9, 0)′	35948 T_1 441	1103	34845 O 439	1126	33719 I_2 438
(0, 10, 0)′	36389 V	1105	35284 Q 416	1127	34157 L_1 446
(0, 11, 0)′	—		35700 S 439	1097	34603 N_1 444
(0, 12, 0)′	—		36139 U	1092	35047 P_1 415
(0, 13, 0)′	—		—		35462 R_1

Analysis.

The analysis of the bands of a polyatomic molecule, in the present state of development, is still to a large extent arbitrary. The total number of bands

and the possible modes of vibration give entirely different possibilities of arrangement. The Raman and infra-red frequencies are of course the guiding factors so far as the ground state of the molecule is concerned, but how these frequencies will be affected as regards intensity and magnitude in the excited

TABLE III.

ω_3'', ω_3' frequencies.

	$(0, 0, 0)''$		$(0, 0, 1)''$		$(0, 0, 2)''$
$(0, 0, 0)'$	33303 G_2 (882)	1366	31937 A_2 (880)		
$(0, 0, 1)'$	34185 L_2 (893)	1368	32817 E_1 (902)	1310	(31507) (886)
$(0, 0, 2)'$	35078 P_2 (892)	1359	33719 I_2 (883)	1326	32393 C_2
$(0, 0, 3)'$	35970 T_2	1368	34602 N_1 (860)		
			35462 R_1		

TABLE IV.

ω_2'', ω_2' frequencies.

	$(0, 0, 0)''$		$(0, 1, 0)''$		$(0, 2, 0)''$
$(0, 0, 0)'$	33303 G_2 (658)	1135	32168 B (668)	1103	(31065) (654)
$(0, 1, 0)'$	33961 K_3 (651)	1125	32836 E_2 (651)	1117	(31719) (659)
$(0, 2, 0)'$	34612 N_2 (672)	1125	33487 H (670)	1109	32378 C_1 (670)
$(0, 3, 0)'$	35284 Q (664)	1127	34157 L_1		33048 F_1 (652)
$(0, 4, 0)'$	35948 T_1				33700 I_1

states of the molecule cannot be predicted with any certainty. In SO_2 in the normal state, three frequencies corresponding to three fundamental modes of vibration are known from Raman and infra-red spectra.[5] These are 525 cm.$^{-1}$ for the symmetric deforming vibration ω_1'', 1146 to 1150 cm.$^{-1}$ for the symmetric valence vibration ω_2'', and 1340 to 1360 cm.$^{-1}$ for the anti-symmetric valence vibration ω_3''. This correlation of the modes of vibration and the triangular shape of the molecule are confirmed by the depolarisation of the Raman frequency 1340 cm.$^{-1}$ The infra-red spectrum indicates 122° as the OSO angle in the ground state. If we accept the band at about 31945 cm.$^{-1}$ as the origin of the system according to Clements, it is possible by using

TABLE V.

$0, 0, v_3'$	$(0, 1, 0)''$	$0, v_2', 0$	$(0, 0, 1)''$
0	32168 B (898)	0	31937 A_2 (669)
1	33066 F_2 (881)	1	32606 D_2 (653)
2	33947 K_2 (898)	2	33259 G_1 (669)
3	34845 O (855)	3	33928 K_1
4	35700 S		
	$(0, 2, 0)''$		$(0, 0, 2)''$
0	(31065) (880)	0	
1	(31945) (899)	1	(31280) (657)
2	32844 E_3 (899)	2	31937 A_2 (660)
3	33743 I_3 (860)	3	32586 D_1
4	34603 N_1		

TABLE VI.

Composite Transitions.

Transitions from *normal state.*

v_2'	$(0, v_2, 0)'$		$(0, v_2, 1)'$		$(0, v_2, 2)'$		$(0, v_2, 3)'$
0	33303 G_2 (658)	882	34185 L_2 (660)	893	35078 P_2 (664)	892	35970 T_2 (683)
1	33961 K_3 (651)	884	34845 O (637)	897	(35742) (647)	911	(36653) (634)
2	34612 N_2 (672)	870	35482 R_2 (657)	907	36389 V	898	37287 W
3	35284 Q (664)	(855)	36139 U				
4	35948 T_1						

the additional bands measured by us on the high frequency side to arrange all of them in such a way that they represent transitions from the vibrational levels of ω_2'' to the levels of ω_2' (*vide* Table II). It will be seen that this gives 1112 cm.$^{-1}$ for ω_2'' in agreement with the Raman frequency 1146 cm.$^{-1}$ and 458 cm.$^{-1}$ for ω_2'. This means that in the excited state of the molecule, the deforming and the symmetric valence vibrations show a uniform decrease in frequency. Thus one of the objections to the earlier analysis would be removed but the objection that the bands form, as it were, two distinct groups in the two regions, remains. Furthermore, the origin will be represented by a weak band, and on the high frequency side there will not be a single band due to a combination transition, involving more than one vibrational mode of the same electronic state.

We have therefore tried a new analysis of the bands on the high frequency side with the idea to test if it is possible to obtain an analysis which introduces for the symmetric valence vibration in the excited state of the molecule a frequency near to that of the excited SO molecule because already in the ground state ω_2'' with 1150 cm.$^{-1}$ is very near to 1118 cm.$^{-1}$ the frequency of SO in the ground state. Indeed, by taking 33303 cm.$^{-1}$ as the origin it has been possible to arrange the bands so that all the bands on the high frequency side are represented as transitions from the low vibrational levels

of the two modes of vibration ω_2'' and ω_3'' to each of the vibrational levels of ω_2' and ω_3' separately and in combination. Tables III to VI contain the analysis and Fig. 2 gives the schematic representation of most of the transitions observed. All the bands have been classified though a few appear to justify classification in two ways. These are also shown in Table I. (The bands in square brackets will be discussed later.) To test whether this analysis can be extended to the low frequency bands listed by Clements we have tried to fit in some of these bands †† as due to transitions arising from the higher vibrational levels of the ground state. This, indeed, appears to be possible as can be seen from the following few examples :—

TABLE VII.

Clements ν in cm.$^{-1}$	Transition
31926	$(0, 0, 2)'' \rightarrow (0, 2, 0)'$
31719	$(0, 2, 0)'' \rightarrow (0, 1, 0)'$
31280	$(0, 0, 2)'' \rightarrow (0, 1, 0)'$
31065	$(0, 2, 0)'' \rightarrow (0, 0, 0)'$
30801	$(0, 1, 2)'' \rightarrow (0, 2, 0)'$
29692	$(0, 2, 2)'' \rightarrow (0, 2, 0)'$

These bands are included in Fig. 2. We feel confident therefore that by using one or two more vibrational levels both in the lower and upper states and with the possibility of combination and composite bands, it will be possible to apply the present analysis to the whole system of bands. This means then, that the bands on the low frequency side are simply an extension of the other bands and the decrease in intensity follows gradually and closely the excitation of the vibrational levels of the ground state. Incidentally, those bands which appear at the extreme end of the visible region will be correlated to higher vibrational levels of the ground level. We intend to continue our work with higher dispersion and greater pressure under different temperatures.

We have not got enough vibrational levels to obtain definite formulæ for the vibrational functions ; this we propose to do later when work on the lower frequency bands is completed. But it can be seen that we obtain

†† These are included in ( ) brackets in Tables II to VI.

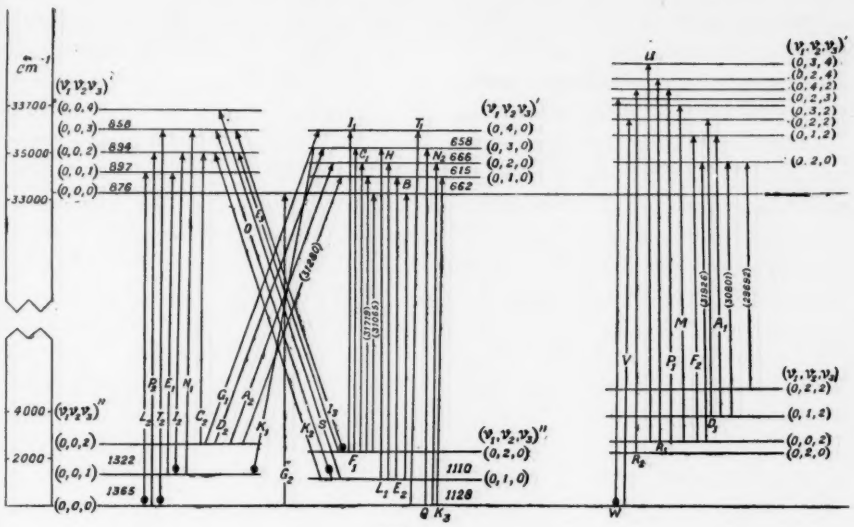

FIG. 2.

ω_2'' and ω_3'' in the ground state and the same two modes of vibration, both with decreased frequency in the excited state of the molecule. These are summarised in Table VIII.

The few vibrational levels in the ground state show decrease in spacing but those in the excited state are not regular. We are not sure how far this is genuine because far from measuring the origins of the bands, here we do not measure even the heads of the bands but only the point of maximum intensity in each band. Even these points of maximum intensity are affected by the overlap of neighbouring band heads. In general, however, the distribution of intensity is more or less normal. The bands may be taken to follow regular progressions, the confused appearance observed by earlier workers being merely due to two modes of vibration being intermixed and to the fact that the 220 cm.$^{-1}$ frequency sought for is not genuine but is roughly the difference between ω_3' and ω_2', which therefore cannot be constant.

The relation between the frequencies of vibration of SO and those of SO_2 is given in Table IX.

This relation indicates that the distance between S and one of the oxygen atoms is increased in the excited state of SO_2, in the same manner as the internuclear distance increases with decreasing ω, on excitation of SO. It appears as if SO_2 in the excited state is no longer isosceles. This agrees with the change in the valence angle OSO, found by Jonescu[6] on a partial rotational analysis of the SO_2 bands. The valency angle of SO_2 decreases from 122° in

TABLE VIII.

Mode of vibration	Level	cm.$^{-1}$
ω_2''	0	0
	1	1128
	2	2238
ω_2'	0	0
	1	662
	2	1312
	3	1978
	4	2636
ω_3''	0	0
	1	1365
	2	2687
ω_3'	0	0
	1	876
	2	1773
	3	2667
	4	3525

TABLE IX.

	SO	SO_2	
	Band Spectra	Infra-red Spectrum	Band Spectra
Unexcited ..	*1118*	525, *1150*, 1360	*1128*, 1365
Excited ..	*623*		*662*, 876

the normal to 96° in the excited state.[6,7] Herzberg and Teller[8] have deduced a rigorous selection rule according to which the antisymmetric frequency should appear if at all as a weak one and only transitions involving an even change between its vibrational levels in the excited and lower electronic states should occur. In the case of a considerable change of internuclear distance on excitation, the rule might be violated in such a manner that also transitions with odd changes in vibrational quantum numbers can take place. But in this case they have to be weak and the transitions should lead either to a forbidden electronic level or to one which involves a forbidden component of electric moment. Since in this case the form of the molecule is completely changed, no definite prediction can be made unless rotational analysis is completed. Furthermore to account for the diffuseness of the bands at shorter wave-lengths which in this case cannot be produced by predissociation for energetical reasons, Franck, Sponer and Teller[9] have assumed that a second electronic level is very near the excited state involved in these bands. Thus a degeneration of the final state of the bands or of certain of its vibrational levels is quite possible.

The analysis given in Tables III, V and VI includes a number of transitions which are forbidden if Herzberg and Teller's selection rules are rigorously valid. These are included in square brackets and some of them appear by no means to be weak. It is, however, possible to classify some of them in such a way that the selection rule is not violated. This is shown in Table X. Fig. 2 displays such of the bands in square brackets as can be classified without violation of Herzberg and Teller's selection principle, as due to the non-forbidden transition. It can be seen that of the seven bands which cannot be classified otherwise (these are marked in Fig. 2) four are either diffuse or weak but three are not so. Too much importance should, however, not be attributed to intensity considerations because as already pointed out above, the main maximum of the envelope of several overlapping bands may be produced in quite different ways and may be due as often as not, to a weak band superimposed on the ascent of a stronger one. This obtains particularly to the group of bands I, since this is a very narrow band made up of at least three different bands. In reality only the band O, one of the few which is not resolved, appears to go against the selection rule. In view of all these considerations, experimental evidence is not definite to decide whether the selection rule is obeyed or violated on account of either degeneration or the complete change which the molecule undergoes on excitation.

It is, however, strange, that the deforming vibration does not appear at all in this electronic transition although it is also a total symmetrical vibration. *A priori* there is nothing known about the frequency of

TABLE X.

Band	Forbidden transition	O—C	Non-forbidden transition	O—C	Remarks
31937 A_2	(0, 0, 1)″ (0, 0, 0)′	− 1	(0, 0, 2)″ (0, 2, 0)′	+ 9	In this case band 31926 A_1 can be classified as (0, 1, 2)″ (0, 1, 2)′, the O—C value being +3.
32606 D_2	(0, 0, 1)″ (0, 1, 0)′	+ 6	(0, 0, 2)″ (0, 3, 0)′	+12	In this case 32586 D_1 can be classified as (0, 1, 2)″ (0, 2, 2)′ with O—C = +13.
33066 F_2	(0, 1, 0)″ (0, 0, 1)′	+15	(0, 0, 2)″ (0, 1, 2)′	+15	
33259 G_1	(0, 0, 1)″ (0, 2, 0)′	+ 9	(0, 0, 2)″ (0, 4, 0)′	+ 7	
33719 I_2	(0, 0, 1)″ (0, 0, 2)′	+ 8			Narrow double superimposed.
33743 I_3	(0, 2, 0)″ (0, 0, 3)′	+11			
33928 K_1	(0, 0, 1)″ (0, 3, 0)′	+12			(Weak).
34185 L_2	(0, 0, 0)″ (0, 0, 1)′	+ 6			(Weak).
34845 O	(0, 1, 0)″ (0, 0, 3)′	+ 3			(Not weak).
35462 R_1	(0, 0, 1)″ (0, 0, 4)′	− 1	(0, 1, 1)″ (0, 3, 3)′ or (0, 0, 2)″ (0, 2, 4)′	− 7 or − 9	
35482 R_2	(0, 0, 0)″ (0, 2, 1)′	− 9	(0, 2, 0)″ (0, 4, 2)′	− 8	
35970 T_2	(0, 0, 0)″ (0, 0, 3)′	0			(Weak).
36139 U	(0, 0, 0)″ (0, 3, 1)′	−18	(0, 0, 2)″ (0, 3, 4)′	−20	Diffuse, uncertain.
37287 W	(0, 0, 0)″ (0, 2, 3)′	+ 5			Diffuse, uncertain.

deformation in the excited level, but in the unexcited it is 525 cm.$^{-1}$ We do not find any vibration in the excited level which might be considered as the

modified value of this frequecy and there is certainly no band at a distance of 525 cm.$^{-1}$ from the origin, which could be considered to be the $(1, 0, 0)'' \rightarrow (0, 0, 0)'$ transition; similar multiples are also absent. In this respect the analysis proposed here certainly does not follow the rules developed by Herzberg and Teller and the question arises if the complete change of form and electric moment of the molecule does not permit even the approximate application of their theory. We have already pointed out, that at present the analysis of such bands is to a large extent arbitrary and it is of course possible to avoid this difficulty by selecting another band as the origin. But then we have to fall back on an analysis like that of Clements or rather the improved one given in the earlier part of this paper (Table II). It is possible then to introduce the total symmetric deforming vibration and to cancel the antisymmetric valence vibration altogether and thus remove all the difficulties mentioned above, but only at the expense of the objections already raised, particularly, the division of the bands into two distinct groups and the weak intensity of the band at the origin. For these reasons and on account of the similarity of ω_2'' and ω_2' with the corresponding values for SO, we prefer the second analysis proposed here in the present state of the development of the theory of polyatomic molecules.

The agreement between the frequencies of the symmetric valence vibration in the ground and the excited states with the corresponding frequencies of the diatomic SO molecule is particularly interesting. From a large amount of chemical and physical evidence, it is known that the bonds in a polyatomic molecule can be approximately considered to be independent of one another. For example, the constant Raman frequencies, the constant values of dipole moments of the same group in different molecules, indicate this. It appears as if this holds good also in the excited state, and as if therefore, the electronic configuration of the one SO bond in SO_2 changes on excitation similarly like that in SO, quite independently of the other SO bond. The wave-mechanical interaction of the two electron pairs of the one double bond with the two of the other bond seems to be very weak and the bond appears to be strongly localised between S and O. Otherwise such a coincidence will be difficult to understand. It might not be too far fetched to suggest that the excited state of SO_2 is brought about by the combination of an unexcited SO molecule ($^3\Sigma$) and an excited oxygen atom (^{1}D), even as the excited state of SO is formed by S (^{3}P)+O(^{1}D). That the energies of the bonds S—Cl, S=O and S=S remain almost unchanged if molecules like S_2 and SO possessing two free valencies combine with other atoms to form polyatomic molecule, *e.g.*, S_2Cl_2, $SOCl_2$ is already shown in discussions on the absorption and photo-dissociation of the chlorides and oxychlorides of sulphur.[4]

The analysis presented here further points out the independence of the bonds not only in the ground state but even in the excited state. At least for the ground state, it can be said that this appears to be rather general. Already a preliminary comparison of band spectroscopic data of diatomic molecules with those of the Raman and infra-red frequencies of polyatomic molecules, reveals a number of examples in which a similarity between the symmetric valence vibrations exists, analogous to the one that exists for internuclear distances.[10] These data are collected in Table XI.

TABLE XI.

Raman effect or Infra-red			Band Spectra	
Molecule	Vibration	(cm.$^{-1}$)	Molecule	ω_e
H_2O	Symmetric valence	3600	OH	3568
$(OH)^-$		3615	,,	,,
CH_4	Total Symmetric valence	2915	CH	2851
$SnCl_4$	,,	365	SnCl	351
PH_3	Valence P—H	2327	PH	~2380
$BiCl_3$	,, Bi—Cl(?)	289	BiCl	308
$SOCl_2$	,, S=O	1229	SO	1118
$POCl_3$	,, P=O(?)	1295	PO	1228
C_2H_4	,, C=C	1623	C_2	1630

As the table shows this relation seems to hold good for non-linear polyatomic molecules with an even number of electrons.

Further investigations on this and related problems are in progress.

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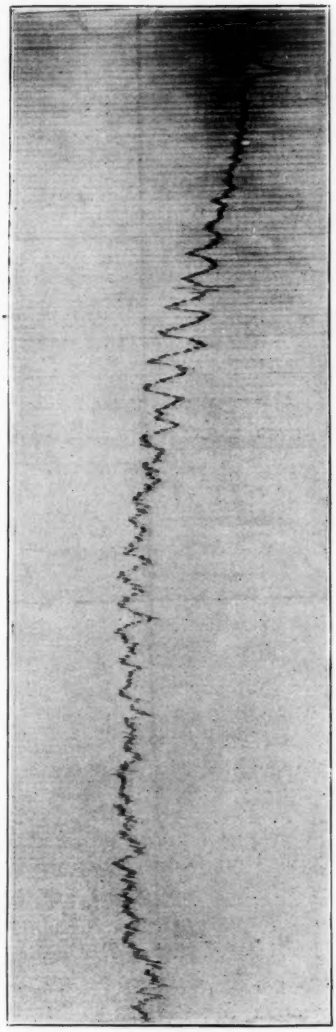

FIG. 1.

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RAMAN SPECTRUM OF CARBON DISULPHIDE.

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1. Introduction.

A detailed study of the Raman spectrum of liquid carbon disulphide is of great importance as it is one of the very few simple molecules that are amenable to such an investigation at ordinary temperatures. Besides a number of earlier workers[1], the following more recent attempts in this direction may be mentioned here. Mesnage[2] employed high dispersion to locate accurately the maxima of various Raman lines. Sirkar[3] studied the dispersion of depolarisation exhibited by them. Langseth, Sorensen and Nielsen[4] also employed high dispersion but obtained results differing markedly from those of Mesnage. The latter authors have examined the intensity and polarisation characters of Raman lines in detail and have raised several important issues regarding their fine structure. None of these investigators, with the exception of Langseth, Sorensen and Nielsen, has stressed the necessity of taking into account the presence of a vibration rotation Raman scattering accompanying the depolarised vibration Raman lines. All these questions are of utmost significance and need to be investigated in great detail in view of the very important recent theoretical work of Fermi[5], Dennison[6] and Placzek[7] relating to the allowed Raman transitions and their mutual intensity relations in the light scattered by linear symmetrical triatomic molecules like CS_2 and CO_2. The present paper is an attempt in this direction and describes some new and interesting results obtained regarding the intensity and polarisation characters of the Raman lines in liquid carbon disulphide. A comparison of the experimental results with the predictions of the existing theories is made.

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[1] See K. W. F. Kohlrausch, *Der Smekal-Raman Effekt*, Julius Springer, 1931.

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[5] *Z. Physik.*, 1931, **71**, 250.

[6] *Phys. Rev.*, 1934, **41**, 304.

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2. *Frequency Shifts.*

The scattered spectrum is photographed for this purpose by means of a 2 prism glass spectrograph of high resolving power employing a slit 0·0075 mm. wide. The instrument has a dispersion of about 30 A per mm. at 4400 A. Alongside the scattered spectrum, is recorded an iron arc spectrum for comparison with the help of which the wave lengths of the various Raman lines are computed. The frequency shifts of the principal line and its satellite obtained by Mesnage, Langseth, Sorensen and Nielsen and the author are given in Table I. The distance between these two lines is of fundamental importance in the theoretical development of the subject referred to earlier and an accurate measurement is therefore repeated here with a view to decide between the conflicting results available.

TABLE I.

Frequency Shifts.

Mesnage	Langseth, etc.	Author
642·6	648·3	648·5
655·5	656·5	655·3

An appreciable discrepancy will be noticed from the results in respect of the smaller frequency shift. The value 648·5 has been obtained by the author for both λ 4046 and λ 4358 excitations and it agrees very well with 648·3 reported by Langseth and others. It is therefore to be concluded that the figure 642·6 due to Mesnage is rather too low.

3. *Structure of the Principal Raman Line.*

An exposure of about 60 hours is given to record the 656 line and its satellite with sufficient density so as to permit of a quantitative investigation of the distribution of intensity being made. A scale of intensity marks is provided on the same plate using a tungsten ribbon lamp fed by a 220 volt battery. The density of the line at different positions and that of the corresponding points in the set of intensity marks is read with the help of a Moll microphotometer and the true distribution of intensity is obtained by drawing the density—log. intensity curves. Fig. 1 represents the curve obtained in this manner and shows an unmistakable breadth of the line besides two prominent peaks which represent the two shifts noted in Table I. A marked similarity may be noticed between this and the curve reproduced by Langseth

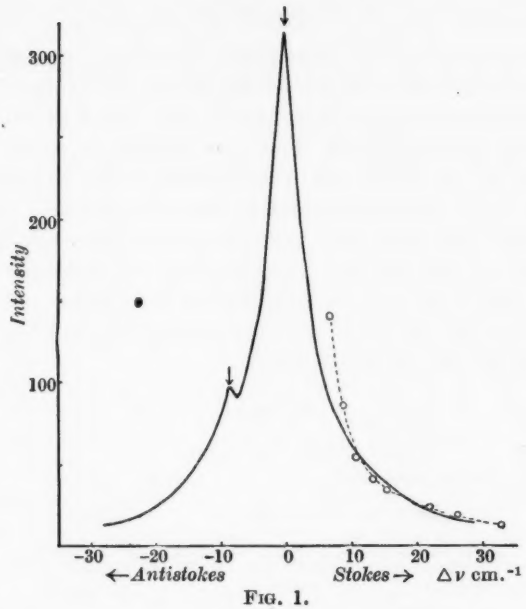

FIG. 1.

and others[8] but the new result which arises out of the present investigation is the recognition of the fact that whereas the principal peak and its satellite marked by arrows are attributable to changes only of the vibrational energy of the molecules, the continuous spectrum on either side of these peaks has not such a simple origin. This is evident from all the well-exposed pictures obtained by the author using a fine slit and is strongly supported by the result, to be discussed more fully in the following sections, that while the peaks show a degree of polarisation which is nearly perfect the continuous spectrum at appreciable distances from the centre exhibits marked depolarisation. This fact suggests a common origin for the complex pattern obtained in Fig. 1 of the 656 Raman line and the nearly completely depolarised continuous wings that are usually obtained on either side of a Rayleigh line in liquids.

The circles in Fig. 1 represent on the same scale the intensity in the wing accompanying the Rayleigh line at corresponding distances obtained by the author in an earlier investigation.[9] The almost exact coincidence of the results in the two cases in the region investigated lends strong support to the views contained in the foregoing paragraph, and the depolarised vibra-

[8] *Loc. cit.*

[9] *Proc. Ind. Acad. Sci.*, 1934, 1, 274.

tion lines, if sufficiently strong, provide us therefore with a convenient method of investigating the special features that characterise this type of Raman scattering in liquids. Such an investigation has been made with this line and the detailed results are under publication elsewhere but the following important features may be noted here. The fact that the satellite at 648 is seen as a well-resolved line in the original plate and as a distinctly separated maximum in Fig. 1 shows clearly that the instrument is capable of detecting any discontinuity or a maximum that may have been present in the wing on the longer wave length side of the central peak as well. It may therefore be concluded that the intensity of the wing associated with the 656 Raman line, as in the case of that accompanying the Rayleigh line, goes on continuously increasing as we approach the centre. For a fuller discussion of the significance of such a result, reference must be made to earlier communications by the author.[10]

4. Depolarisation and Dispersion of Depolarisation of the Raman Lines.

A glass condenser is used for this purpose to illuminate the liquid contained in a wide tube and the scattered light is separated into horizontal and vertical components by a suitably oriented double image prism. The two components are focussed one above the other on to the slit of the spectrograph and are photographed simultaneously and for the same time. As has already been pointed out by earlier investigators, such an arrangement would give rise to errors due mainly to lack of strict transversality between the directions of incidence and observation and oblique refraction at the surfaces of the prisms. Corrections for these errors are introduced in the usual manner[11] and the ratio of intensities of the horizontal and the vertical components of each one of the Raman lines is determined with the help of graded intensity marks given on the same plate by the method of varying slit widths. Two independent plates have been obtained using a slit width of 0·015 mm. and the mean values are given in Table II.

For the 656 Raman line excited by λ 4358, earlier investigators have reported values ranging from 0·3 to 0·15. Amongst these, Langseth, Sorensen and Nielsen have given the lowest value, *viz.*, 0·15 which is in excellent agreement with that obtained by the author. For the 796 line, they have reported 0·18 which is somewhat less than the depolarisation given in Table II. It must be noted here that the figures given above have been arrived at only by comparing the peak intensities and the results therefore represent the state of polarisation of the Q branch which is nearly but not quite completely

[10] *Ind. Jour. Phys.*, 1933, **8**, 437 and subsequent papers.

[11] S. Bhagavantam, *Ind. Jour. Phys.*, 1932, **7**, 79.

TABLE II.

Depolarisation Values.

Exciting line ..	λ 4358		λ 4046	
Raman line ..	656	796	656	796
Depolarisation ..	0·15	0·24	0·20	..

free from the accompanying continuous wing. The wing on the other hand exhibits a large depolarisation and as it has already been pointed out in the present investigation no separate maximum or a discontinuity in it has been detected. This fact of its intensity continuously increasing as we reach the centre of the Q branch obviously complicates matters and shows that the depolarisation value depends to a large extent on the slit width employed and the resolving power of the instrument. Discrepancies between the results obtained by various investigators in the past may be ascribed to this fact. The presence of such a continuous spectrum which appears to be inseparable from the Q branch proper, contrary to the case of gases, makes all quantitative determinations of either the intensity or the polarisation characters of depolarised lines somewhat uncertain as one is unable to say how much of the energy is actually in the Q branch itself.

An important result that may be noticed from Table II is the dispersion of depolarisation of the 656 Raman line. Amongst the investigators already referred to, only Sirkar has studied this aspect of the problem but the results obtained in this paper are in marked disagreement with those reported by him. He obtained values of ρ which are in the ratio of 1 : 0·85 : 0·75 for the 656 line excited by λ 5460, 4358 and 4046 respectively. The figures indicate a marked dispersion in which the depolarisation of the line *increases* with *increasing wave length*. The present investigation shows on the contrary an equally marked dispersion but in the opposite direction, *i.e.*, the depolarisation *increases* with *diminishing wave length*. Analogy with Rayleigh scattering suggests that the result reported by Sirkar is highly improbable but the origin of such a discrepancy is not clear.

5. *Intensity of Raman Lines.*

Pienkowski[12] reported that the intensities of the 656 and 796 lines are in the ratio of 3·1 : 1 whereas Langseth, Sorensen and Nielsen obtained a

[12] *Acta. Phys. Pol.*, 1932, **1**, 87.

value of 12·7 : 1 under high dispersion comparing only the peak intensities of these lines. The latter authors have however obtained a ratio of 3 : 1 in good agreement with the result of Pienkowski by regarding the areas under the curves and not the peaks as representing the intensities. Under low dispersion* they have obtained a ratio of 8·3 : 1. These discrepant results indicate that the experimental conditions regarding the dispersion and resolution are of utmost importance in determining the intensity ratios. In the present investigation, a high resolving power instrument already referred to and a fine slit are employed. The relative intensities of the peaks as well as the total areas under each one of the lines have been determined with the help of density-log. intensity curves drawn from a scale of intensity marks provided on the same plate by the method of varying slit widths. Four different plates have been obtained and the figures arrived at by averaging the results are given in Table III. The quantitative results so far available from other investigators and the experimental conditions under which these have been obtained are also included in the table for comparison.

TABLE III.

Intensity Relations.

Authors	Experimental Conditions	Peak int. 656 / Peak int. 796	Total area 656 / Total area 796
Pienkowski	Unknown	..	3·1
Langseth and others	Dispersion : 7A./mm. at 4400A. Slit width : 0·03 mm. Satellites well separated from the main lines.	12·7	3·0
,,	Dispersion : Low. Slit width : 0·05 to 0·1 mm. Satellites not separated from the main lines.	8·3	..
Veerabhadra Rao	Dispersion : 30A./mm. at 4400A. Slit width : 0·015 mm. Satellites well separated from the main lines.	9·2	6·6

It may be noticed from Table III that although the conditions employed by the author are such that the satellites are well resolved from the main

* The conditions referred to here are such that the satellites are not separated from the main lines and are therefore less favourable than those prevailing in the present investigation.

lines, the ratio of peak intensities is obtained as 9·2, in better agreement with the result reported by Langseth and others working under low dispersion than that obtained by them under high dispersion. On the other hand, there is a marked discrepancy between the ratio of the total areas as obtained by the author and Langseth and others.

The theoretical interpretation of the Raman spectrum of carbon sulphide worked out fully by Placzek[13] based on the earlier ideas of Fermi and Dennison leads to the following approximate relation which is of great importance in checking the validity of the theory and establishing an inter-relationship between the intensities and the frequency shifts of the various Raman lines.

$$\frac{|[a]^{00}_{02}|^2}{|[a]^{00}_{10}|^2} = \frac{|(\sqrt{x-}\,|\,\Delta\,|\,a_1 \mp \sqrt{x+}\,|\,\Delta\,|\,a_2)|^2}{|(\sqrt{x+}\,|\,\Delta\,|\,a_1 \pm \sqrt{x-}\,|\,\Delta\,|\,a_2)|^2} \quad .. \quad .. \quad (1)$$

In the above expression x is equal to $\sqrt{\Delta^2+8P^2}$ where Δ and P are quantities which are simply related to the frequency shifts of the main lines and their satellites. The left hand side represents the ratio of intensities of the Q branches of the 796 and 656 lines and, as has already been remarked in the section on frequency shifts, the author's measurements are in close agreement with those of Langseth, Sorensen and Nielsen and hence it is assumed that $\Delta = -120$ cm.$^{-1}$ and $|P| = 17{\cdot}8$ cm.$^{-1}$ as has been calculated by the latter authors. These are to be preferred to $\Delta = -106$ and $|P| = 33$ given by Placzek on the basis of Mesnage's measurements. Substituting 1/9·2, the ratio of intensities of the peaks, for the expression on the left hand side of equation (1) and the above values of Δ and $|P|$ we get $\frac{|a_1|^2}{|a_2|^2}$ equal to 69 which is of the same order of magnitude and compares well with the expected ratio 100 : 1.

6. *Discussion of Results.*

Amongst the new and important results that have been reported in the foregoing sections, mention may be made here of the distribution of intensity in the wing accompanying the principal vibration line 656. The results which clearly show that separate maxima in the PP and RR branches do not exist, cast doubt on some recent attempts to ascribe closely spaced broad bands in liquids to such an origin.*

The observation that the depolarisation of the 656 line *increases* with *decreasing wave length* of the exciting radiation is also of special significance.

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[13] *Loc. cit.*

* See Langseth, Sorensen and Nielsen, *Loc. cit.*, p. 409.

Calculations† based on the doublet theory of optical anisotropy of molecules[14] have shown that the depolarisation of Rayleigh scattering as well as that of the principal Raman line has a tendency to *increase* but very slowly with *decreasing wave length* of the exciting radiation. On the basis of this theory it is also deduced that the depolarisation of the Q branch of the principal line excited by λ 4358 should be 0·25 which may be compared with the observed value 0·15 given in Table II. Thus the experimental results, while showing a qualitative agreement both in respect of the dispersion of depolarisation and its absolute magnitude with the predictions of the doublet theory, are not capable of being quantitatively deduced in such a simple manner.

The slightly higher depolarisation of the 796 line in comparison with that of the 656 line may be noted. This result is in agreement with the earlier report of Langseth and others.

In conclusion the author wishes to express his grateful thanks to Mr. S. Bhagavantam for his constant help and interest during the progress of this work.

7. *Summary.*

A detailed investigation has been made of the intensity and polarisation characters of the Raman lines in carbon disulphide. It is found that the Q branch of the principal vibration line 656 cm.$^{-1}$ cannot be separated from the PP and RR branches. The intensity distribution in the latter is similar to that obtained in the wings accompanying the Rayleigh lines in liquids. This line, when excited by λ 4358, exhibits a depolarisation of 0·15 and the value increases to about 0·2 if the exciting wave length is λ 4046. The ratio of intensities of the peaks of 656 and 796 Raman lines has been found to be 9·2 whereas the ratio of the total areas under these lines is obtained as 6·6.

† Details of the calculation are omitted here for want of space.

[14] K. R. Ramanathan, *Proc. Roy. Soc.*, 1925, **107**, 684; and S. Bhagavantam, *Ind. Jour. Phys.*, 1931, **6**, 557.

ON THE ARITHMETICO-LOGICAL SYMMETRIC FUNCTIONS OF n ATTRIBUTES.

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In the statistical theory of attributes[1] a double order of ideas is used. In the first place the logical calculus is applied to the attributes, so that the symbol (AB) represents the logical product of the attributes A and B; that is, (AB) means, by definition, the attribute possessed by, and only by, those elements of the universe of discourse, that possess simultaneously the attributes A and B. In a similar manner, $A \oplus B$ representing the logical sum of A and B, is the attribute possessed by, and only by, those elements of the universe which possess at least one of the attributes A, B. These two fundamental operations of the logical calculus are associative and commutative[2]; further each of them is distributed by the other, so that, contrary to what happens in the case of the arithmetical sum and the arithmetical product, there is a dual symmetry between the properties of these two operations. For example, the fundamental law of absorption $a \oplus a\,b = a$, in the logical calculus is paralleled by $a\,(a \oplus b) = a$, which is obtained by interchanging the two operations.

In the second place, in the statistical theory each attribute-symbol A is made to represent also the number (supposed to be finite) of elements of the universe of discourse, which possess the attribute A. This permits attribute-symbols to be subjected to the arithmetical operations of addition and subtraction, in addition to the logical operations of addition and multiplication. By this double-edged use of the symbolism, the formulæ of the theory of attributes are able to represent definite numerical relations, instead of being merely qualitative, as those of the logical calculus.

In this paper this double use of the symbolism will be adopted, and the methods of the logical calculus will be utilised to study the properties of what I call the *logico-symmetric functions*, and the *arithmetico-logical symmetric functions* of n attributes $A_1, A_2, \cdots, A_n$. Particular cases of these properties are known, but the general results and their applications I

[1] See Yule's *Introduction to the Theory of Statistics*, Part I.

[2] See Whitehead's *Universal Algebra*, or any book on Symbolic Logic.

believe to be new. We shall begin by a compact formulation and proof of two known results.

§1. The logical sum of n attributes $A_1, A_2, \cdots, A_n$ can be expressed in terms of their logical products, by means of arithmetical operations. The precise expression is:

THEOREM I. $A_1 \oplus A_2 \oplus \cdots \oplus A_n = \Sigma A_1 - \Sigma (A_1A_2) + \Sigma (A_1A_2A_3) - \cdots$,

where Σ's represent always arithmetical sums.

Proof. An element of the universe which possesses exactly t of the n attributes is enumerated $\binom{t}{1}$ times in the first term of the right-hand side, $\binom{t}{2}$ times in the second term, $\binom{t}{3}$ times in the third and so on. Hence the number of times it is enumerated on the right-hand side is:

$$\binom{t}{1} - \binom{t}{2} + \binom{t}{3} - \cdots = 1 - (1-1)^t$$
$$= \begin{cases} 0, & \text{if } t = 0 \\ 1, & \text{if } t > 0. \end{cases}$$

Thus any element which actually possesses one or more of the attributes A is enumerated exactly once on the right, and also exactly once in the logical sum of the n attributes. Hence the result.

From the symmetric relation between logical addition and logical multiplication, we may expect an analogous expression for the logical product of the n attributes in terms of their logical sums. We have in fact:

THEOREM II. $(A_1A_2 \cdots A_n) = \Sigma A_1 - \Sigma S_{12} + \Sigma S_{123} - \Sigma S_{1234} + \cdots$,

where $S_{pqr\ldots}$ denotes $A_p \oplus A_q \oplus A_r \oplus \cdots$

Proof. An element which possesses exactly t of the attributes is enumerated t times in the first term on the right, $\binom{n}{2} - \binom{n-t}{2}$ times in the second term, $\binom{n}{3} - \binom{n-t}{3}$ times in the third term, and so on. Hence the number of times it is enumerated on the right is:

$$\left[\binom{n}{1} - \binom{n}{2} + \cdots\right] - \left[\binom{n-t}{1} - \binom{n-t}{2} + \cdots\right]$$
$$= (1-1)^{n-t} - (1-1)^n$$
$$= \begin{cases} 1, & \text{if } t = n \\ 0, & \text{otherwise.} \end{cases}$$

Thus every element is enumerated the same number of times on the right as in the logical product on the left. Hence the result.

§2. *The elementary logico-symmetric functions of* $A_1, A_2, \cdots, A_n$.

By analogy with the algebraic theory of symmetric functions, we may define *the* rth *elementary logico-symmetric function* a_r of $A_1, A_2, \cdots, A_n$, to be the logical sum of their $\binom{n}{r}$ logical products r at a time. Thus the logical sum and the logical product of $A_1, A_2, \cdots, A_n$ are respectively their first and nth logico-symmetric functions. The following simple properties of the logico-symmetric functions a_r should be noted:

(*a*) *The* rth *symmetric function* a_r *of* $A_1, A_2, \cdots, A_n$ *is not only the logical sum of their logical products* r *at a time, but also the logical product of their logical sums* $n-r+1$ *at a time.*

For, the logical sum a_r of the logical products r at a time of $A_1, A_2, \cdots, A_n$, enumerates exactly once every element e of the universe which possesses at least r of the attributes $A_1, A_2, \cdots, A_n$. It is clear that these elements e are precisely those that possess one attribute at least out of every set of $n-r+1$ attributes chosen from $A_1, A_2, \cdots, A_n$; (for example, if an element e' possesses less than r of the attributes A, it is obvious that we can choose at least one set of $n-r+1$ attributes A, none of which is possessed by e'). Thus the elements e are precisely those that are enumerated without repetition and exception by the logical product of the logical sums $n-r+1$ at a time of $A_1, A_2, \cdots, A_n$, which proves our statement.

(*b*) There is a relation of implication between any two attributes represented by the symmetric functions a, so that the logical sum and product of any two a's may be immediately written down. We have in fact:

$$\left.\begin{aligned} a_p \oplus a_q &= a_p \\ (a_p\, a_q) &= a_q \end{aligned}\right\} \text{ if } p \not> q.$$

These are obvious from the meaning of the logical operations and the definition of the a's. If we use the ordinary geometric interpretation adopted in the logical calculus, the attributes $a_1, a_2, \cdots, a_n$ will correspond to n regions each of which contains the next.

It follows from these equations that the distinct values of the logical products r at a time of $a_1, a_2, \cdots, a_n$ are $a_r, a_{r+1}, \cdots, a_n$. Hence the logical sum of these logical products is a_r. In other words the attributes $a_1, a_2, \cdots, a_n$ are in order their own successive symmetric functions. It follows that $a_1, a_2, \cdots, a_n$ are the only symmetric functions of $A_1, A_2, \cdots, A_n$ that can be derived purely by means of the two logical operations.

§3. *The Arithmetico-logical symmetric functions of* $A_1, A_2, \cdots, A_n$.

If however we are permitted to use arithmetical addition over and above the two logical operations, then every expression of the form:

$$a_1\,\alpha_1 + a_2\,\alpha_2 + \cdots + a_n\,\alpha_n,$$

where $a_1, \cdots, a_n$ are positive or negative integers, is a symmetric function of $A_1, A_2, \cdots, A_n$; strictly speaking, it does not represent an attribute but an enumerating process carried out by means of the attributes. Conversely, we may shew that any arithmetico-logical symmetric function S of the attributes $A_1, A_2, \cdots, A_n$ can be represented as a linear function with integer coefficients, of $\alpha_1, \alpha_2, \cdots, \alpha_n$. For since by hypothesis S is a symmetric function of $A_1, A_2, \cdots, A_n$, the number of times S (t) which it enumerates an element e possessing t of the attributes A, does not depend on which of the attributes A are possessed by e, but only on the number t. The symmetric function S is therefore completely characterised[3] by the n non-negative integers $S(1), \cdots, S(n)$. Now, the number of times which an element possessing t of the attributes A is enumerated by $a_1\alpha_1 + a_2\alpha_2 + \cdots + a_n\alpha_n$ is $a_1 + a_2 + \cdots + a_t$. Hence S must be identical with $S(1)\ \alpha_1 + \{S(2) - S(1)\}\ \alpha_2 + \cdots + \{S(n) - S(n-1)\}\ \alpha_n$. We have thus expressed an arbitrary arithmetico-logical symmetric function S as a linear form with integer-coefficients in $\alpha_1, \alpha_2, \cdots, \alpha_n$.

Among the arithmetico-logical symmetric functions of $A_1, A_2, \cdots, A_n$, the functions A_r^p are of fundamental importance. *We define* A_r^p *to be the arithmetic sum of the* $\binom{n}{r}$ *p*th *logico-symmetric functions of sets of r attributes chosen from* $A_1, A_2, \cdots, A_n$. This definition implies that $p \not> r$. It is clear that $A_n^p = \alpha_p$; apart from the functions α, there are $\binom{n}{2}$ functions A_r^p. Since A_r^p can be expressed as a linear form in the α's, we may write

$$A_r^p = \sum_s a_{rs}^p\ \alpha_s.$$

THEOREM III. $a_{rt}^p = \binom{t-1}{p-1} \cdot \binom{n-t}{r-p}$, so that $a_{rt}^p = 0$, if $t < p$ or $> n - r + p$.

Proof. The number of times which an element possessing exactly t of the attributes A, is enumerated by A_r^p is equal to the number of r-combinations of the n attributes which contain at least p of the t attributes. This number is evidently:

$$A_r^p\,(t) = \binom{t}{p}\binom{n-t}{r-p} + \binom{t}{p+1}\binom{n-t}{r-p-1} + \cdots$$

[3] It is assumed that the symmetric function does not enumerate the elements of the universe, which possess none of the attributes A.

Also:

$$a_{rt}^{p} = A_r^p(t) - A_r^p(t-1)$$
$$= \binom{t-1}{p-1}\binom{n-t}{r-p}.$$

It follows that A_r^p can be expressed in terms of $n-r+1$ of the logico-symmetric functions, namely, $a_p, a_{p+1}, \cdots, a_{n-r+p}$.

In particular,

$$A_r^r = a_r + \binom{r}{1} a_{r+1} + \binom{r+1}{2} a_{r+2} + \binom{r+2}{3} a_{r+3} + \cdots + \binom{n-1}{n-r} a_n.$$

$$A_r^1 = \binom{n-1}{r-1} a_1 + \binom{n-2}{r-1} a_2 + \cdots + a_{n-r+1}.$$

It follows that the determinant of the $n-r+1$ functions $A_r^r, A_{r+1}^{r+1}, \cdots, A_n^n$, *qua* linear forms in $a_r, a_{r+1}, \cdots, a_n$ is unity. It follows that a_p can be expressed, for $p \geqslant r$ as an integral linear form in $A_r^r, A_{r+1}^{r+1}, \cdots, A_n^n$.

The actual expression is given by:

THEOREM IV. $a_r = A_r^r - \binom{r}{1} A_{r+1}^{r+1} + \binom{r+1}{2} A_{r+2}^{r+2} - \cdots$

For, the coefficient of a_{r+t} on the right is

$$\binom{r+t-1}{t} - \binom{r}{1}\binom{r+t-1}{t-1} + \binom{r+1}{2}\binom{r+t-1}{t-2} - \cdots$$

$$= \text{coefficient of } x^t \text{ in } (1+x)^{r+t-1}(1+x)^{-r} = (1+x)^{t-1}$$

$$= \begin{cases} 0, & \text{if } t > 0 \\ 1, & \text{if } t = 0, \end{cases} \text{ which proves the result.}$$

Similarly, $A_r^1, A_{r+1}^1, \cdots, A_n^1$ are linear forms in $a_1, a_2, \cdots, a_{n-r+1}$, with determinant ± 1. Hence a_{n-r+1} is an integral linear form in $A_r^1, \cdots, A_n^1$. We have:

THEOREM V. $a_{n-r+1} = A_r^1 - \binom{r}{1} A_{r+1}^1 + \binom{r+1}{2} A_{r+2}^1 - \cdots$

For the coefficient of $a_{n-r+1-t}$ on the right is:

$$\binom{r+t-1}{r-1} - \binom{r}{1}\binom{r+t-1}{r} + \cdots$$

$$= \text{Coefficient of } x^t \text{ in } (1+x)^{r+t-1}(1+x)^{-r} = (1+x)^{t-1}$$

$$= \begin{cases} 0, & \text{if } t = 0 \\ 1, & \text{if } t > 0 \end{cases}, \text{ which proves the result.}$$

More generally the forms $A_r^p, A_{r+1}^{p+1}, \cdots A_n^{n-r+p}$ are $n-r+1$ linear forms with non-vanishing determinant in $a_p, a_{p+1}, \cdots, a_{n-r+p}$. Hence a_p can be expressed as a linear form in $A_r^p, A_{r+1}^{p+1}, \cdots, A_n^{n-r+p}$. We have in fact:

THEOREM VI. $\binom{n-p}{r-p} a_p = A_r^p - \binom{p}{1} A_{r+1}^{p+1} + \binom{p+1}{2} A_{r+2}^{p+2} - \cdots$

Proof. The coefficient of a_{p+t} on the right is:

$$\binom{n-p-t}{r-p} \cdot \left[\binom{p+t-1}{t} - \binom{p}{1}\binom{p+t-1}{t-1} + \binom{p+1}{2}\binom{p+t-1}{t-2} - \cdots\right]$$

As before, the part within square brackets is equal to 1 or 0, according as $t = 0$ or > 0. This proves the result.

In the same way, the forms A_r^p, A_{r+1}^p, $\cdots$, A_n^p are $n-r+1$ linear forms with non-vanishing determinant in a_p, a_{p+1}, $\cdots$, a_{n-r+p}. Hence a_{n-r+p} can be expressed linearly in terms of them. We have in fact:

THEOREM VII. $\binom{n-r+p-1}{p-1} a_{n-r+p} = A_r^p - \binom{r-p+1}{1} A_{r+1}^p + \binom{r-p+2}{2} A_{r+2}^p - \cdots$

Proof. The coefficient of $a_{n-r+p-t}$ on the right is:

$$\binom{n-r+p-t-1}{p-1}\left[\binom{r-p+t}{r-p} - \binom{r-p+1}{1}\binom{r-p+t}{r-p+1} + \cdots\right]$$

The part within square brackets is, as before, equal to 1 or 0, according as $t = 0$ or $t > 0$. This proves the result.

Theorem VI is an extension of Theorem IV, which is itself an extension of Theorem I; similarly Theorem VII is an extension of Theorem V, which is itself an extension of Theorem II.

§4. *Application to* n *real numbers.*

Let A_1, A_2, A_3, $\cdots$, A_n be n real numbers represented by points A_1, A_2, $\cdots$, A_n on a straight line. Choose a point O on the line to the left of all the points A, and let d_i = the distance OA_i. Let the universe of discourse be a set of points to the right of O, whose distances from O are integral multiples of an infinitesimal (ϵ). Let now A_i represent also the attribute of lying between O and A_i. It is then clear that the number A_i is proportional to the distance d_i. Also the numbers corresponding to (A_iA_j) and $A_i \oplus A_j$ are clearly proportional to the lesser and the greater of the two distances d_i, d_j. Hence the logical product and the logical sum of A_i, A_j correspond respectively to the less distant from O, and the more distant from O, of the two points A_i, A_j. If we denote by $R^{\lambda}_{pqr\ldots}$, that one among the points A_p, A_q, A_r, $\cdots$ which is the λth in order from the right, it is clear that the point $R^{\lambda}_{pqr\ldots}$ corresponds to the λth logico-symmetric function of A_p, A_q, A_r, $\cdots$. Similarly $I^{\lambda}_{pqr\ldots}$, which is the λth in ascending order of magnitude of the k real numbers A_p, A_q, $\cdots$, or the λth in order from

the left of the k points $A_p, A_q, \cdots$, corresponds to $(k-\lambda+1)$th logico-symmetric function of $A_p, A_q, \cdots$

We shall now state the forms which our previous theorems take for this concrete instance of the calculus:

THEOREM I. $R^1_{12\ldots n}$ = the greatest of the numbers $A_1, A_2, \cdots, A_n$

$$= \Sigma A_1 - \Sigma L^1_{12} + L^1_{123} - \Sigma L^1_{1234} + \cdots$$

THEOREM II. $L^1_{12\ldots n}$ = the least of the numbers $A_1, A_2, \cdots, A_n$

$$= \Sigma A_1 - \Sigma R^1_{12} + \Sigma R^1_{123} - \Sigma R^1_{1234} + \cdots$$

THEOREM IV. $R^r_{12\ldots n}$ = the rth in descending order of magnitude of the numbers $A_1, A_2, \cdots, A_n$,

$$= \Sigma L^1_{12\ldots r} - \binom{r}{1} \Sigma L^1_{12\ldots(r+1)} + \binom{r+1}{2} \Sigma L^1_{12\ldots(r+2)} - \cdots$$

THEOREM V. $L^r_{12\ldots n}$ = the rth in ascending order of magnitude of the numbers $A_1, A_2, \cdots, A_n$

$$= \Sigma R^1_{12\ldots r} - \binom{r}{1} \Sigma R^1_{12\ldots(r+1)} + \binom{r+1}{2} \Sigma R^1_{12\ldots(r+2)} - \cdots$$

THEOREM VI. $\binom{n-p}{r-p} R^p_{12\ldots n} = \binom{n-p}{r-p} \times$ the pth in descending order of the numbers A,

$$= \Sigma L^{r-p+1}_{12\ldots r} - \binom{p}{1} \Sigma L^{r-p+1}_{12\ldots(r+1)} + \binom{p+1}{2} \Sigma L^{r-p+1}_{12\ldots(r+2)} - \cdots$$

THEOREM VII. $\binom{n-p}{r-p} L^p_{12\ldots n} = \binom{n-p}{r-p} \times$ the pth in ascending order of the numbers,

$$= \Sigma R^{r-p+1}_{12\ldots r} - \binom{p}{1} \Sigma R^{r-p+1}_{12\ldots(r+1)} + \binom{p+1}{2} \Sigma R^{r-p+1}_{12\ldots(r+2)} - \cdots$$

We may make now a formal extension of these results. Let an ordered set of m real numbers $(a_1, a_2, \cdots, a_m)$ be called an m-dimensional vector with the components $a_1, a_2, \cdots$. Given n vectors $A_1, A_2, \cdots, A_n$ with the components $A_i = (a_{i1}, a_{i2}, \cdots, a_{im})$, we can determine a vector $B_r = (b_{r1}, b_{r2}, \cdots, b_{rm})$ whose kth component b_{rk} is the rth in descending order of magnitude of the numbers $a_{1k}, a_{2k}, \cdots, a_{nk}$ $(k = 1, 2, \cdots, m)$. We shall term the vector B_r in a purely formal manner, *the* r*th descending composite*

of the n vectors $A_1, A_2, \cdots, A_n$. We similarly define *the* rth *ascending composite* of $A_1, A_2, \cdots, A_n$ as the vector whose kth component is the rth in ascending order of magnitude of the numbers $a_{1k}, a_{2k}, \cdots, a_{nk}$. We may denote the rth descending and ascending composites of $A_p, A_q, \cdots$ by $R^r_{pq\ldots}$, $L^r_{pq\ldots}$. Then, *the following vector equations hold*, which are of the same form as those established for numbers:

THEOREM VI $$\binom{n-p}{r-p} R^p_{12\ldots n} = \Sigma\, L^{r-p+1}_{12\ldots r} - \binom{p}{1} \Sigma\, L^{r-p+1}_{12\ldots(r+1)} + \cdots$$

THEOREM VII $$\binom{n-p}{r-p} L^p_{12\ldots n} = \Sigma\, R^{r-p+1}_{12\ldots r} - \binom{p}{1} \Sigma\, R^{r-p+1}_{12\ldots(r+1)} + \cdots$$

For, the corresponding equations have been established for any particular component of all the vectors involved.

These equations and the concept of the rth ascending and descending composites of n vectors will find application in the theory of the g.c.d. and l.c.m. of a set of integers.

§5. *The greatest common divisor and least common multiple.*

Every integer which does not involve prime factors other than a given finite set of primes $(p_1, p_2, \cdots, p_m)$, may be represented in the form $p_1^{a_1} p_2^{a_2} \cdots p_m^{a_m}$, where $a_1, a_2, \cdots, a_m$ are positive integers or zero. Thus each such integer may be represented by a vector $(a_1, a_2, \cdots, a_m)$ in such a way, that the product of two such integers is represented by the vector-sum of the corresponding vectors. Also it is clear that the g.c.d. and l.c.m. of a number of such integers $A_1, A_2, \cdots, A_n$ (say), is represented the first ascending composite, and the first descending composite of the corresponding vectors. Let g_1 be the g.c.d. of $A_1, A_2, \cdots, A_n$ and let g_r be the g.c.d. of the l.c.m.'s r at a time of $A_1, A_2, \cdots, A_n$. The series of numbers $g_1, g_2, \cdots, g_n$ may be called the first, second, $\cdots$ rth, $\cdots$ g.c.d.'s of $A_1, A_2, \cdots, A_n$. It is clear that g_n is the l.c.m. l_1 of $A_1, A_2, \cdots, A_n$. We may similarly define l_r to be the l.c.m. of the g.c.d.'s r at a time, and call l_r the rth l.c.m. of $A_1, A_2, \cdots, A_n$. It is clear that the vector corresponding to g_r is the rth ascending composite of the vectors corresponding to $A_1, A_2, \cdots, A_n$, and that the vector corresponding to l_r is the rth descending composite of the same vectors.

Since the rth ascending composite of n vectors is the $n-r+1$ descending composite of the same vectors, it follows that $g_r = l_{n-r+1}$.

Denote the kth g.c.d. and kth l.c.m. of $A_p, A_q, A_r \cdots$ by $g^k_{pqr\ldots}$ and $l^k_{pqr\ldots}$ respectively. Since the addition and subtraction of vectors correspond to the multiplication and division of the corresponding numbers, we see that the two vector relations of last para would lead to multiplicative

expressions for l_p and g_p in terms of the $(r-p+1)$th g.c.d.'s and the $(r-p+1)$th l.c.m.'s respectively of subsets of the n numbers. The actual expressions are:

THEOREM VI. $$(l_p)^{\binom{n-p}{r-p}} = \frac{\pi g_{12\ldots r}^{r-p+1} \cdot \left(\pi g_{12\ldots(r+2)}^{r-p+1}\right)^{\binom{p+1}{2}} \cdot \left(\pi g_{12\ldots r+4}^{r-p+1}\right)^{\binom{p+3}{4}} \ldots}{\left(\pi g_{12\ldots(r+1)}^{r-p+1}\right)^{p} \cdot \left(\pi g_{12\ldots(r+3)}^{r-p+1}\right)^{\binom{p+2}{3}} \ldots}$$

THEOREM VII. $$(g_p)^{\binom{n-p}{r-p}} = \frac{\pi l_{12\ldots r}^{r-p+1} \cdot \left(\pi l_{12\ldots(r+2)}^{r-p+1}\right)^{\binom{p+1}{2}} \cdot \left(\pi l_{12\ldots(r+4)}^{r-p+1}\right)^{\binom{p+3}{4}} \ldots}{\left(\pi l_{12\ldots r+1}^{r-p+1}\right)^{p} \cdot \left(\pi l_{12\ldots r+3}^{r-p+1}\right)^{\binom{p+2}{3}} \ldots}$$

These relations are very general. Their particular cases are:

THEOREM IV. $$l_p = \frac{\pi g_{12\ldots p}^{1} \cdot \left(\pi g_{12\ldots p+2}^{1}\right)^{\binom{p+1}{2}} \ldots}{\left(\pi g_{12\ldots(p+1)}^{1}\right)^{p} \cdot \left(\pi g_{12\ldots(p+3)}^{1}\right)^{\binom{p+2}{3}} \ldots}$$

THEOREM I. $$l_1 = \frac{A_1 A_2 \ldots A_n \cdot \pi g_{123}^{1} \cdot \pi g_{12345}^{1} \ldots}{\pi g_{12}^{1} \cdot \pi g_{1234}^{1} \ldots}$$

and relations of the same form with l and g interchanged.

HINDERED ROTATION AND OSCILLATION OF MOLECULES IN LIQUIDS AND IN CRYSTALS.

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Received June 22, 1935.

1. Introduction.

Extensive experimental investigations by Weiler,[1] Trumpy,[2] Rousset,[3] Ranganadham,[4] Bhagavantam[5] and Veerabhadra Rao[6] on the rotational Raman effect in liquids have brought to light certain characteristic features which are not in agreement with the predictions of the existing theories. This is probably connected with the fact that the latter are all based on the assumption of freely rotating molecules, a condition which is presumably not fulfilled in liquids or dense fluids. Nevertheless, liquids do exhibit wings on either side of the Rayleigh lines which are apparently connected with the optical anisotropy of the molecules. These must therefore be interpreted as Raman radiations arising in a manner which in some respects at least is analogous to the origin of rotational Raman scattering in gases. A satisfactory explanation of these phenomena is of fundamental importance from the point of view of the liquid state, and for this purpose, a new suggestion is made in the present paper which is based on some ideas put forward by the author in an earlier communication.[5] A brief review of the other explanations that have so far been offered is also presented.

2. Characteristics of Rotational Raman Scattering in Liquids.

In the communications referred to above, it has been shown that the intensity of the rotation wing in all the liquids studied, with the exception of liquid hydrogen, starts from being a maximum at or very near the centre of the Rayleigh line, falls off rapidly till a certain distance is reached and then only gradually fades away lingering on to such distances as are wholly irreconcilable with the view that the entire wing is due to single and normally rotating molecules. The existing theories, on the other hand, predict that the intensity should start from being zero near the centre, increase till a certain point is reached where the wing exhibits a maximum intensity and then fall off somewhat abruptly. Thus the experiments differ from the theoretical results in three important respects, *viz.*, (i) absence of a maximum of intensity at a specified point well separated from the centre, (ii) concentration of intensity in the neighbourhood of the centre, (iii) extension of the wing to large distances from the centre.

In two communications Gross and Vuks[7] have recently published results of great significance in this connection. They find that the continuous spectrum in the remoter regions of the wings exhibited by diphenyl ether, benzene and naphthalene in the liquid state is replaced by separate lines in the Raman spectra of these substances when studied in the solid state. In addition, the continuous spectrum close to the Rayleigh line altogether disappears in all these cases as we pass from the liquid to the solid state.

3. Explanation of the Results.

The author has attempted to account for the observed results in liquids in an earlier paper already referred to, by assuming that the molecules in a liquid are arranged in a quasi-crystalline manner, the crystalline arrangement being akin to that which is present in the corresponding solid state. Forces similar to those in the crystal will exhibit between the neighbouring molecules of the liquid and an extension of Pauling's[8] work on "The Rotation of Molecules in Crystals" at once tells us that the liquids can in general be divided into two classes : one set of liquids, examples of which are liquid hydrogen, nitrogen, oxygen, etc., in which most of the molecules are freely and normally rotating in spite of the quasi-crystalline arrangement, the other set of liquids, examples of which are molten iodine, benzene and others composed of heavy molecules, in which most of the molecules are executing only small oscillatory motions about their equilibrium positions which may be called incomplete rotations. The quasi-crystalline forces in these cases hinder free rotation and the oscillatory motion can pass over into a complete rotation only if the temperature is sufficiently high. It has been suggested that these oscillatory motions which are very imperfectly quantised in liquids are responsible for the extended regions of the so-called rotation wings, and the recent results of Gross and Vuks lend strong support to such a view. As soon as the substance is crystallised the oscillations become definitely quantised and appear as separate lines in the scattered light. Further evidence in support of this view which will be presented in this paper is as follows.

Pauling's theory permits us to make a rough computation of the frequencies that are to be expected.* Taking the specific case of benzene, it is seen that its specific heat reaches a value of 5 cal/grm. mol., at a temperature of 34·5° K. This would mean that $h\nu_0/k$ for benzene is 103·5° K where h and k have the usual significance and ν_0 represents the frequency of oscillation. From this ν_0 may be evaluated as 72 cms.$^{-1}$ Gross and Vuks have actually observed two lines at 63 cms.$^{-1}$ and 108 cms.$^{-1}$ The

* For details of computation, see L. Pauling, *Phys. Rev.*, 1930, **36**, 430.

order of magnitude is very satisfactory in view of the assumptions involved and the fact that the benzene crystal is not a cubic one may be responsible for the splitting up of the oscillation into two different frequencies.

Moreover, the idea of an incomplete rotation at once shows that just as in the case of normally rotating molecules, the optical anisotropy will play an important part in deciding the intensities of these lines. This conclusion is in accordance with the observed fact that such extended wings are usually exhibited prominently only by substances like benzene, naphthalene, carbon disulphide, etc., which are highly optically anisotropic.

It must be pointed out here that the explanation offered by Gross and Vuks that they are due to "vibrations characteristic of crystalline lattice" is essentially different from the foregoing views. In the opinion of the author, such lattice oscillations are different and examples of the same can be found in the Raman spectra of calcite, aragonite, etc. A serious defect of such an explanation is that one does not see any obvious relationship between the intensity of the corresponding Raman scattering and the optical anisotropy of the substance, whereas experimental results clearly show that only strongly anisotropic substances exhibit this phenomenon either as lines in solids or as continuous and extended wings in liquids.

4. Summary.

The extended portion of rotation wings in liquids and the separate lines which take their place in the corresponding solids are explained as due to small oscillatory motions of molecules about their equilibrium positions. The motion is properly quantised in solids on account of the perfect crystalline arrangement and results in distinctly separated lines possessing definite frequency shifts. In liquids, there is only an imperfect quantisation on account of the quasi-crystalline arrangement and this results in a broadening of the lines into a continuous wing. A rough computation of the oscillation frequency in benzene from the specific heat data on the lines indicated by Pauling gives 72 cms.$^{-1}$ which is of the expected order of magnitude. These oscillations, as pictured by Pauling, may be regarded as incomplete rotations and such a picture involves a direct relationship between the optical anisotropy of the molecule and the intensity of the scattered line. This is in accordance with the experimental fact that only substances like benzene and naphthalene which have a marked degree of anisotropy give rise to extended wings in the liquid state and lines in the solid state.

In conclusion the author desires to express his grateful thanks to Professor Sir C. V. Raman for his kind interest in the work.

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SOME ASPECTS OF GROSS INTENSITIES IN ELECTRONIC BANDS WITH SPECIAL REFERENCE TO C_2 (SWAN) AND N_2 (SECOND POSITIVE) SYSTEMS.

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1. Introduction.

The subject of spectral intensities is one of the most difficult in modern spectroscopy and one which has received very little attention at the hands of experimental physicist. However, with the researches of Dorgelo[1] in the field of atomic spectra in the years 1923 and 1924, the study of relative intensities of spectral lines entered on a new stage of development. After the enunciation by Burger and Dorgelo[2], in 1924, of the sum rule for intensities in a line multiplet, the interest in the subject has grown very rapidly and it has been actively investigated among others by Ornstein and Burger and their colleagues in the University of Utrecht.

As the experimental results advanced, it was found that the sum rule which followed closely upon the modern concepts of quantum mechanics, was found to agree better in some atomic series, but in others it was merely an approximation. But on the whole it served as a useful guide. In other fields also, *viz.*, the X-rays and the Zeeman patterns, the intensities follow closely the theoretical formulæ developed for optical line spectra.

In the sphere of molecular spectra the sum rule was found to be applicable to intensities with the retention of exponential Boltzmann factor. The intensity factors for heavy symmetric molecules derived theoretically by Hönl and London[9], by using the matrix and wave-mechanics were found to agree with the sum rule. With the quantitative estimation of intensities for different series in helium bands, Johnson and Turner[6] have recently succeeded in verifying Bonger's formula of Balmer series with certain modifications. The knowledge of intensities within the structure of a band enables us to assign certain "effective temperatures" to emitting gas as evidenced from the results of Ornstein and Van Wijk[3] on the negative nitrogen (N_2^+) bands and of Kapuscinski and Eymers[4] on the mercury hydride bands. These methods have also been extended by Richardson[5] (R.S.) to stellar bodies to know their "effective temperatures". It may therefore be said that as far as

the structure lines of an individual band are concerned, the results are in many cases in accordance with the predictions of theory.

When it is a question of gross intensities of several bands in a system, the problem becomes different. On account of the large spectral ranges involved in this branch, the experimental work is often very difficult. Theoretical ideas in this connection began to be advanced in the year 1925, with the explanation by Franck[7], of the mechanism of dissociation of molecules by light absorption. Condon[8] extended the ideas to electronic bands and by means of his theory, now known as Franck-Condon principle, predicted certain general characteristics of intensity distribution in a system. Quantitative work on vibrational intensities is very little. Confirmation of Franck-Condon theory was a sort of semi-quantitative data mostly obtained as eye-estimates. With a view to get, therefore, accurate data, a programme of intensity measurements was undertaken by us at London with the latest and improved experimental technique. From experimental standpoint, this problem of vibrational intensities appears more promising, on account of the ease with which the band heads could be photographed in preference to rotational structure lines. The investigation of even an empirical relation between temperature and gross intensities, might lead to the application of band spectroscopic methods to problems in astro-physics.

2. The Problem.

Quantitative investigations into gross intensities in band systems were undertaken in Utrecht in 1930, by Elliott[10] who made accurate measurements on bands of β-system of boron oxide (BO) and latterly on the α-system.[11] Ornstein and Brinkman[12] have measured the intensities of violet CN-system with a view to determine the temperature of carbon arc. Wurm[13] in Potsdam has also determined the intensity distribution in the absorption bands of CN and C_2 (Swan) systems as obtained in R- and N-type stars. In our programme of work we undertook the measurements in C_2 (Swan)[15] and N_2 (Second positive)[16] systems, both produced under a variety of experimental conditions, and the results of which have since been published. Herzberg[14] has also made an attempt to measure the intensities of 2nd positive and negative bands of N_2, but his results do not appear to have been obtained with the rigorous technique of heterochromatic photometry.

It is known that conditions of excitation play a prominent part in producing or isolating certain spectra. It is from this standpoint that some aspects, not hitherto touched, of our results on C_2 and N_2 bands will be studied in the present paper. Reference will also be made to certain relevant features of CN-violet system[17], the improved results on which are awaiting publication.

3. *Experimental.*

The methods and technique of intensity measurement have been sufficiently dealt with in a paper by Read and L. W. Johnson[18] and in a subsequent paper by Johnson and author.[15] It is therefore deemed unnecessary to enter here into any of those details. It is believed, however, that the results of intensity measurements on which interpretations have been based in the present paper are accurate enough to justify the conclusions drawn. By way of illustration discrepancy between eye-estimates and accurate microphotometric results in N_2 (Second positive) system can be judged from the following figure (Fig. 1). Similar results have been obtained for Swan

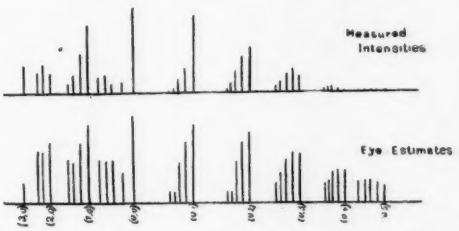

FIG. 1. Comparison of eye-estimates with measured intensities (N_2 second positive).

system. Comparison shows that our visual results are generally over-estimated by several hundred per cents.

4. *Results and Discussion.*

For a normal distribution of intensity in a band system, the 0—0 band is the strongest, the intensity falling rapidly for other bands in that sequence. For bands of other sequences, the intensities gradually diminish, the point of maximum intensity shifting from the first band to bands of higher v' v'' values. The band systems under study are said to have normal distribution and this has been verified by our experimental results. In Figs. 2 and 3 are drawn the slopes of relative intensity fall or rise in sequences of both systems. One point, however, that requires special mention, is in regard to 0—0 sequence of N_2. In this the intensity falls rapidly at first upto (2, 2) and then rises suddenly at (3, 3) in all the sources except the spark where the rise is found at (4, 4) band. It is difficult to understand this unless we assume two Condon parabolas of distribution with their apex at (0, 0) and (3, 3) respectively. But in the absence of bands having values above $v'=4$, this is impossible to study.

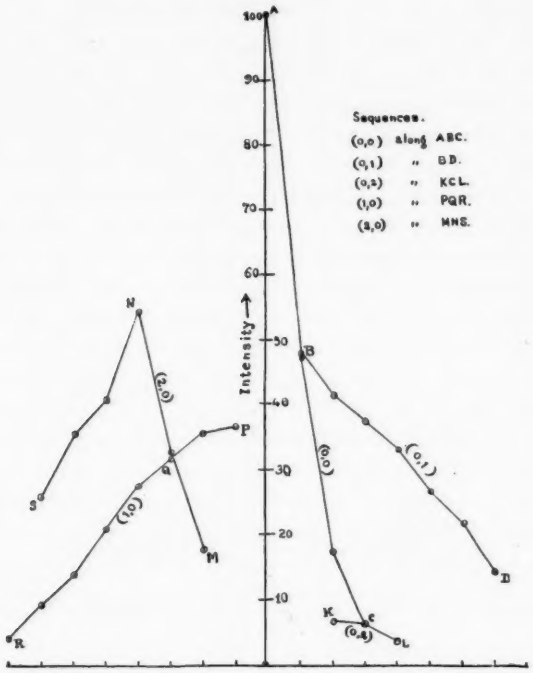

FIG. 2. Relative intensity slopes in sequences of C_2 (Swan) system.

According to equation

$$I/\nu^4 = A.p_{v'v''}.e^{-\frac{E_{v'}}{kT}}$$

the function $\sum_{v'} I/\nu^4$ for the initial levels should diminish as we go to higher v' values if the temperature equilibrium holds. This appears to be true in both C_2 and N_2, for all conditions except the argon discharge, where the Swan bands are excited in about 30 mms. pressure of the inert gas. Here the log $\Sigma I/\nu^4$ is shown as a function of $E_{v'}$, the vibrational energy of initial levels (Fig. 4). The graph is quite unusual giving a parabolic shape with apex at about $v'=2$. This distribution is obscure in its origin and if genuine, will have to be explained, apart from temperature, probably as a specific effect of the inert gas resulting from unknown collision processes.

In each sequence, if the log of band intensity divided by ν^4 is proportional to $E_{v'}$, we should expect statistical equilibrium of molecules with their surroundings at a particular temperature. Whether this holds in the case of arc

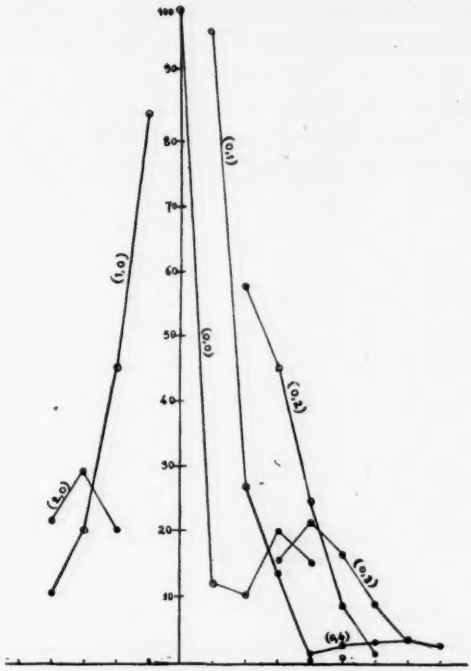

FIG. 3. Relative intensity slopes in sequences of N_2.

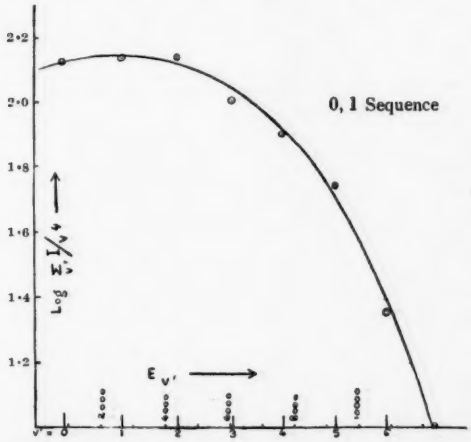

FIG. 4. Log $\sum_{v'} I_{v'v''}$ as a function of $E_{v'}$ for Swan bands in argon.

which is generally classed with flames, we have drawn graphs showing log $I/_{\nu^4}$ of each band of sequence against $E_{v'}$ of the Swan and CN violet systems both produced in carbon arc, the former in presence of hydrogen. Similar figures have also been constructed for oxy-coal-gas flame excitation. (See Figs. 5 to 9.) One is led to conclude from these figures that a thermal distribution nearly prevails for cyanogen in arc, as is the case with oxy-coal-gas flame

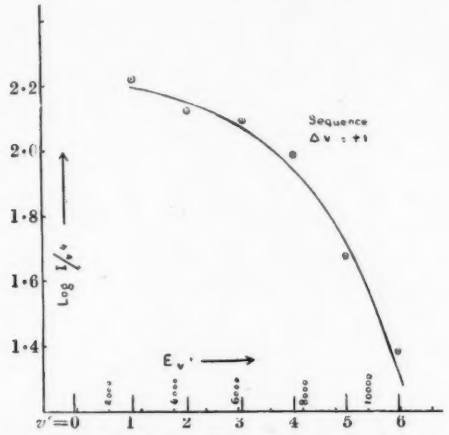

FIG. 5. Log $I/_{\nu^4}$ as a function of $E_{v'}$ in sequences of Swan bands in arc.

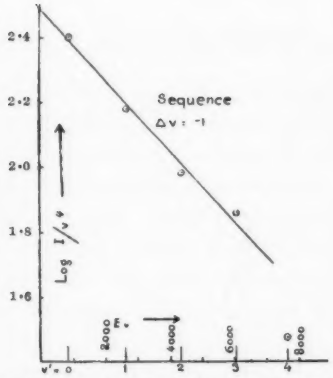

FIG. 6. Log $I/_{\nu^4}$ as a function of $E_{v'}$ in sequences of Swan bands in arc.

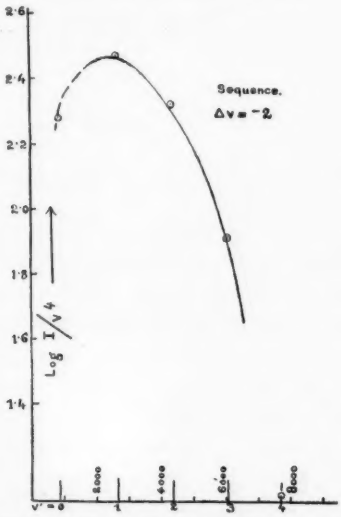

FIG. 7. Log $I/_{\nu^4}$ as a function of $E_{v'}$ in sequences of Swan bands in arc.

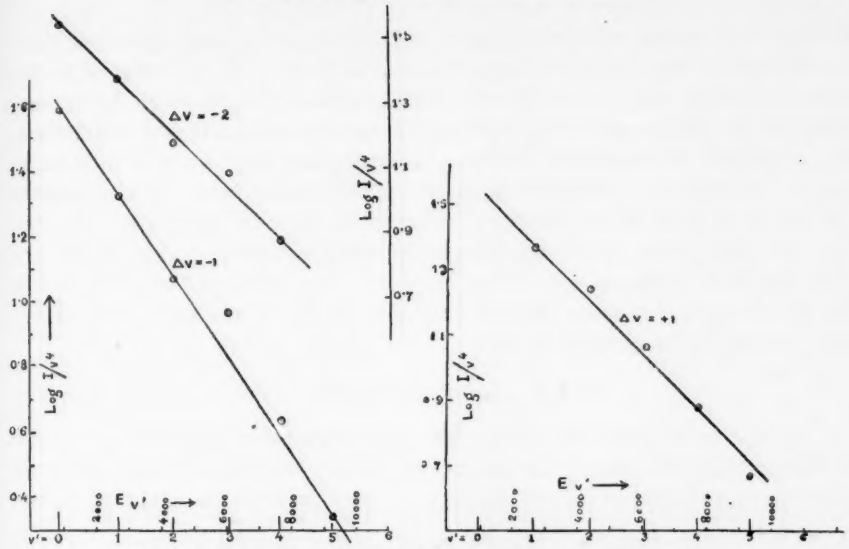

FIG. 8. Log I/ν^4 in sequences of C_2 (Swan) in oxy-coal-gas flame.

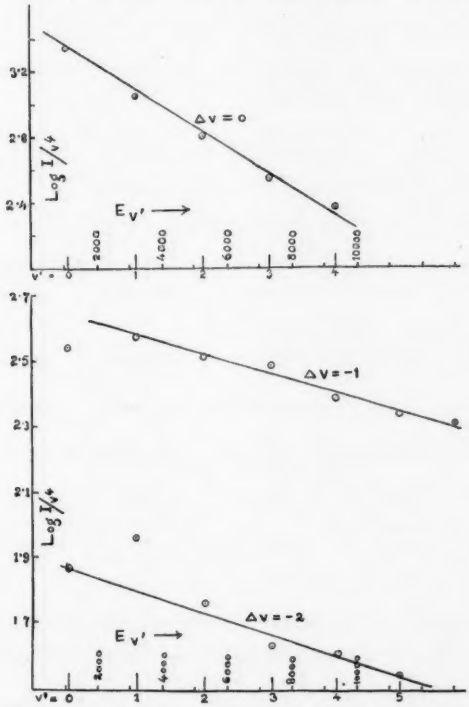

FIG. 9. Log I/ν^4 in sequences of CN-system in arc.

though the values of temperatures derived on this basis give no clear evidence of it. Its absence in Swan bands in arc, which can be deduced by the nature of graph, may be attributed to the formation of C_2 molecule from more complex molecular groupings, energy changes in which are not understood. Consequently the excitation of Swan bands in arc may be non-thermal in origin. Its presence in CN-system is a likely consequence of the greater affinity of carbon to atmospheric nitrogen at high temperatures. In discharge tubes where low temperature conditions prevail, the CN bands are only obtained in presence of active nitrogen. The discharge in low pressure air with carbon electrodes or with carbon as impurity generally gives bands of CO molecule (Ångstrom bands).

5. *Intensity Centres.*

In the next treatment, the Swan bands have been particularly chosen to discuss the positions of maxima of intensities. In various sequences from the observed values of band intensity and wavelength, we could form the quantity

$$=\bar{\lambda}\frac{\Sigma I\lambda}{\Sigma I}$$

according to procedure adopted by Johnson.[19] $\bar{\lambda}$ may be described as the "optical centre of gravity" or the "centre of intensity" of the sequence. Such results are given below in Table I.

TABLE I.

Positions of "Intensity Centres".

C_2 (Swan System).

Sequence	Spark	Arc	Bunsen flame	Oxyflame	Argon
2, 0 ..	4370·3	4370·2	4370·8	4373·2	4374
1, 0 ..	4715	4709·7	4712·6	4713·1	4706
0, 0 ..	5155·6	5154·5	5155·3	5157	5147·5
0, 1 ..	5580·3	5582·0	5586·3	5585	5557·4
0, 2 ..	6044	6105·7	6100·9	6099·3	6035

With the extension of the same reasoning, we have also calculated the "Intensity Centre" of the Swan system in the different sources.

The values are tabulated below in Table II.

TABLE II.

Condition of excitation	Intensity centre $\bar{\lambda}$
Spark under glycerine ..	5075
Arc in H_2 ..	5190
Bunsen flame ..	5252
Oxy-coal-gas flame ..	5252
Argon discharge ..	5355

Fig. 10 shows how the "intensity centre" shifts from one condition to the other in sequences as well as in the whole system. Assuming the approximate temperatures as follows, *viz.*, Argon discharge 600° K, flame 2200° K, arc 4000° K, and spark 6500° K, some of which have been determined by different

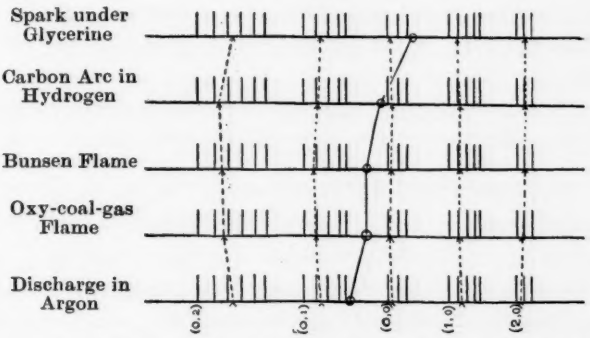

FIG. 10. " Intensity Centres " in sequences and in the system (Swan Bands of C_2).

N.B.—Dotted line passing through " Centres " in sequences. Full line across for " Centres " in the system.

authors by spectroscopic or other methods, a graph is drawn showing these against wavelength of the "intensity centre" ($\bar{\lambda}$) of the whole system. This is given in Fig. 11. It appears from this that $\bar{\lambda}$ of the "intensity centre" is some function of temperature within the sources, the exact form of which cannot be clearly defined.

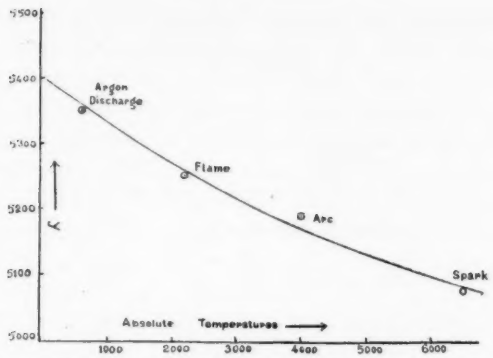

FIG. 11. Wavelength of "Intensity Centres" and temperatures of sources. (C_2 Swan system.)

Taking the two thermally excited sources, *i.e.*, bunsen and the oxy-coal-gas flames, we get the same $\bar{\lambda}$ for both. If the temperature difference between these be of the order of $\pm 500°$, we may not expect an appreciable redistribution of intensity, and this may account for the same "centre" found for both. It may be noted in this connection that the temperatures derived for these by Johnson and Tawde[15] on the assumption of Boltzmann distribution of vibrational energy in the excited state, also give a common value for both, *viz.*, 4700°K. although this cannot be the real temperature in either of these two sources.

Another point which may be mentioned is the relative total "weights" of levels in the different sources, derived by taking the sum of $\sum_{v'} I/\nu^4$ of all the levels. These are found in the ratios,

Bunsen flame,	Arc,	Spark,	Oxy-flame,	Argon
1	: 1·052	: 1·073 :	1·205	: 2·341

which can be taken as those of radiating molecules in the different sources. Argon again offers here a point of special interest.

6. *Transition Probabilities.*

Irrespective of the conditions of excitations, the *maximum* transition probabilities generally obey the Franck-Condon principle. Such a result is to be expected as Condon's theory does not take into account the distribution of molecules in the initial states. Any discrepancy between theory and experimental results is to be sought in the degree of accuracy of the nuclear potential energy function defining the potential curves. The values of maximum transitions derived by the use of Morse function[20]

$$U(r) = D_e (e^{-2ax} - 2e^{-ax})$$

closely agree with experimental values as may be seen from the following Table :

TABLE III.

Most Probable Transitions in C_2 (Swan).

r_{max} → r_{max}		r_{min} → r_{min}	
Theoretical	Experimental	Theoretical	Experimental
1, 0	1, 0	0, 2	0, 1
2, 1	2, 1	1, 3	1, 3
3, 2	3, 2	2, 4	2, 4
..	4, 3	3, 6	3, 5
5, 4	5, 4	4, 7	4, 6
6, 5	6, 5	5, 8	5, 7
7, 6	7, 6		

But this function does not satisfy the transitions observed in BeO by Johnson and Dunston[24] and N_2 (Second positive) bands by Tawde.[23] They approximate to theoretical values derived from Rydberg function,[21]

$$U(r) = D_e (ax+1)e^{-ax}.$$

Nothing in favour of one or the other can be said at present unless we are in possession of more experimental material.

Leaving aside the maximum probabilities, we shall now discuss the effect of conditions of excitation on the relative probabilities of transition in various v''-progressions. In Figs. 12 to 15 are plotted these results for C_2 (Swan) system.

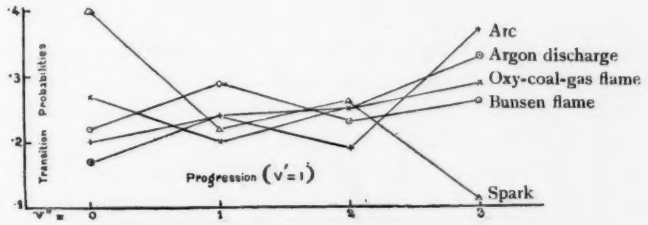

FIG. 12. Transition probabilities in v''-progressions (C_2).

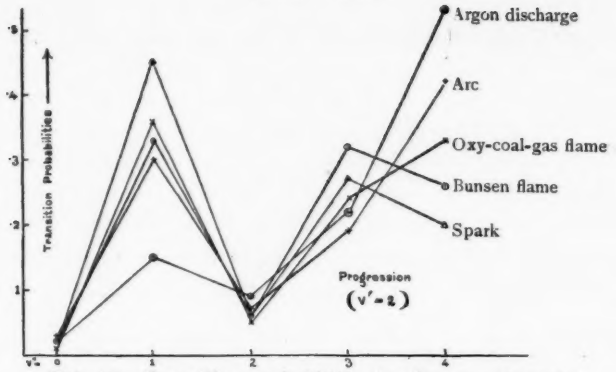

FIG. 13. Transition probabilities in v''-progressions (C_2).

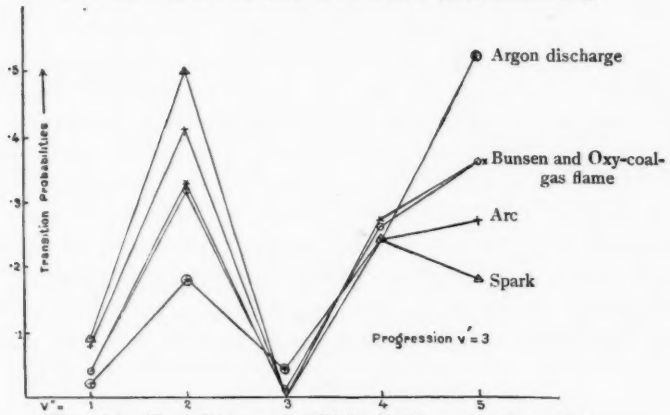

FIG. 14. Transition probabilities in v''-progressions (C_2).

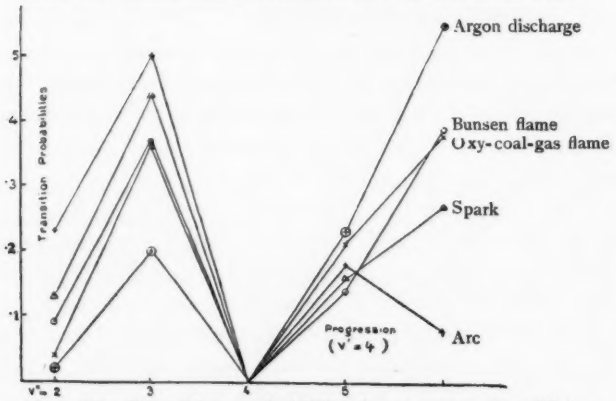

FIG. 15. Transition probabilities in v''-progressions (C_2).

From a study of these figures, it may be concluded that the radiating C_2 molecules in argon tend to favour levels above $v''=4$. The transitions in the spark, on the other hand, are more or less of opposite nature, the molecules in this case preferring levels below $v''=4$. This is particularly noticeable upto progression $v'=3$. But above this, the arc conditions begin to predominate and we get in the latter case, the bands (4, 2), (5, 4) and (6, 5) to have very high probabilities. The corresponding highly probable transitions in argon are $5\rightarrow7$ and $6\rightarrow8$.

Purely thermal conditions such as the bunsen flame or the oxy-coal-gas flame do not show such selective behaviour probably on account of the steady nature of excitation as against the violent one of electrical conditions like spark.

In the case of spark under glycerine, the transitions $0\rightarrow0$, $1\rightarrow0$, $2\rightarrow1$, $3\rightarrow2$, are very high in comparison to others. The fact is that C_2 molecule is formed here from a more complex hydro-carbon molecule like glycerine. It is believed that in the dissociative process which goes on in the spark, the radiating C_2 molecules find themselves in the intense electrical fields of neighbouring charged atoms especially of hydrogen and these may cause their early dissociation giving more probable transitions for the above bands.

To come again to argon, it offers a special problem for study. Here the levels $v''=4, 5, 6, 7, 8$ are favoured more than others, as pointed out already, giving higher probabilities for bands (2, 4), (3, 5), (4, 6), etc. It may be remarked that the production of these bands in preference to others is characteristic of argon which brings out spectra of low energy conditions. Johnson and Cameron[22] have investigated the effect of argon and other inert gases on certain molecular spectra and they classify this effect under three heads: (i) isolation of spectra difficult to obtain otherwise; (ii) redistribution of spectral energy, usually towards the red; and (iii) reduction of broadening of lines. Out of these, the effect observed in Swan bands under study may be classed under (ii). This can be verified from the position of "intensity centre" at longer λ 5355 relative to others. We shall revert to this subject of argon in the following paragraph when dealing with nitrogen.

In the case of nitrogen, the most probable transitions which follow from Condon's theory are verified to nearer approximation, only by the use of Rydberg function as said elsewhere. With regard to relative values of these in v''-progressions two of which are given in Figs. 16 and 17, the high probability for $2\rightarrow1$ transition in argon has been suggested by the author in a recent paper[16] as a consequence of Heitler and London level in its neighbourhood, being not favoured by N_2 molecules in presence of the inert gas.

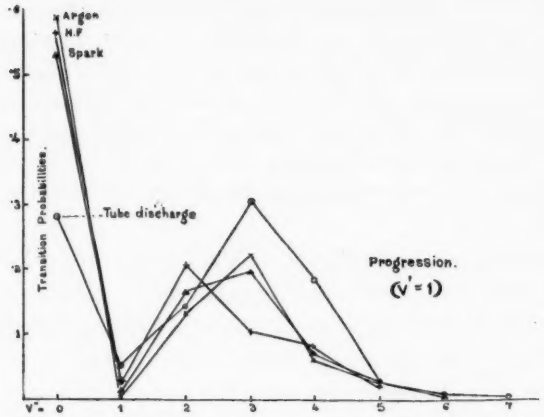

FIG. 16. Transition probabilities in v''-progressions (N_2).

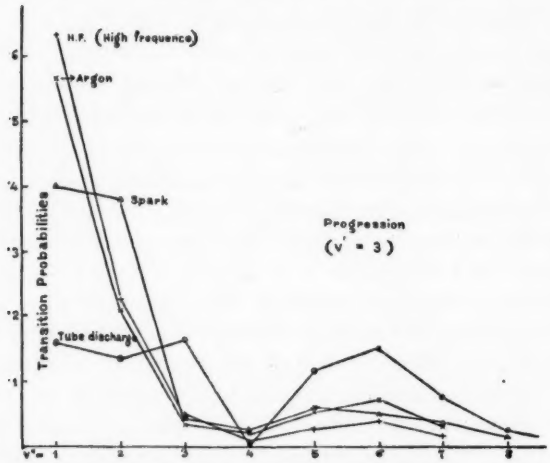

FIG. 17. Transition probabilities in v''-progressions (N_2).

Another point which requires to be noted here is the absence of transition $4 \rightarrow 3$ in argon in spite of its high value in other sources. The same source also gives a very high probability for transition $(4 \rightarrow 2)$. According to quantum theory, the action of inert gas may be described as increasing the probability of those orbits which correspond to smaller energy quanta. With argon present in such large proportions (99% to 0·7% N_2) at a pressure of about 40 mms., we may expect this to happen under the present conditions But it is surprising to note that unlike Swan bands in argon, we get here

some evidence of energy displacement towards the violet end instead of towards the longer wavelengths. This can be seen from high values of probabilities obtained for transitions $1 \rightarrow 0$, $2 \rightarrow 1$, $3 \rightarrow 1$ and $4 \rightarrow 2$. The effect might be analogous to one observed by Johnson[19] in the first positive system of this molecule, where for a trace of nitrogen in argon, the energy displacement towards the more refrangible end is of the order of 30 to 40 A.U. Determination of the "centres of intensity" in various sources will furnish some additional material for interpretation, but it has been found impossible to complete it within the scope of this paper.

Summary.

(1) The development of the subject of spectral intensities to gross intensities of bands has been reviewed.

(2) The Swan system of C_2 and N_2 (second positive) systems have been chosen to treat some aspects relating to the conditions of excitation.

(3) The probabilities of transition, the temperatures, and the "centres of intensity" have been discussed in relation to each other where possible.

(4) Attempt has been made to explain some unusual intensity features of bands excited in different sources especially in argon.

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THE ENTROPY OF MANGANOUS AMMONIUM SULPHATE AT TEMPERATURES CLOSE TO ABSOLUTE ZERO, IN RELATION TO THE MAGNETIC ANISOTROPY OF THE SALT AT ROOM TEMPERATURES.

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In a recent paper on the production of very low temperatures by the adiabatic demagnetization method of Debye and Giauque, Kürti and Simon[1] obtain the following important result. If T_i be the initial temperature and H_i the magnetizing field, and if T_f be the final temperature obtained by adiabatically demagnetizing the salt to zero field, then

$$\frac{T_f}{T_i} = \frac{E_m}{E_i} = \frac{k\theta_m}{H_i g\beta}, \qquad \ldots \quad (1)$$

where E_i is the difference in energy between the adjacent m-levels split by the magnetic field H_i; $E_i = H_i g\beta$, g being the Landé factor and β the Bohr magneton. E_m is a certain small energy, characteristic of the crystal in zero magnetic field, which will be of the order of magnitude of the Stark-splitting of the energy levels of the paramagnetic ion under the crystalline fields. The corresponding *characteristic temperature* θ_m is defined by the relation

$$k\theta_m = E_m, \qquad \ldots \quad (2)$$

in which k is the Boltzmann constant. If we assume that the crystalline Stark-splitting is into $(2J+1)$ equally spaced energy levels, then $k\theta_m$ would be the energy difference between adjacent levels.

θ_m is thus an important constant, which determines the deviation of the magnetic entropy of the crystal from its ideal value of $R \log_e (2J+1)$, and therefore defines the entropy-temperature curve at these temperatures. Any method that would enable us to calculate θ_m would therefore be of great interest. Its calculation from the actual Stark-splitting is not easy, since we do not have, at present, sufficient knowledge of either the magnitude

[1] *Proc. Roy. Soc.* (A), 1935, **149**, 152.

or the dissymmetry of the crystalline fields. Kürti and Simon[2] have suggested an indirect method of calculating θ_m, namely, from the anomaly of the specific heat of the crystal, which begins to appear at temperatures considerably higher than θ_m. For example from measurements on the specific heat of gadolinium sulphate in the range 2°–5° K, they were able to calculate the value of its θ_m, which has since been verified by direct demagnetization experiments on the substance.

The purpose of the present note is to draw attention to another and more convenient method of calculating θ_m, namely from measurements on the magnetic anisotropy of the crystal at *room temperatures*. Let us take as an example the well-known monoclinic Tutton salt $MnSO_4.(NH_4)_2SO_4.6H_2O$. Though, to a first approximation, the crystal is magnetically isotropic and its susceptibility obeys the Curie law, as we should expect from the circumstance that the ground state of the Mn^{++} ion is an S-state ($^6S_{5/2}$), careful measurements reveal a feeble anisotropy.[3] A small part of this anisotropy is that of its diamagnetism, which will be practically the same as that of the isomorphous diamagnetic Tutton crystal obtained by replacing the Mn by Mg or Zn ; it can therefore be corrected for. Another small correction also is necessary, namely, for the anisotropy of the Lorentz-Poisson magnetic polarisation field acting on the Mn^{++} ions in the crystal, the anisotropy being due to the non-cubic distribution of these ions. The residual anisotropy of the manganous salt, after making these two corrections, should evidently be attributed to the feeble Stark-splitting of the S-levels of Mn^{++} in the crystal, *i.e.*, to the same mechanism which is responsible for the diminution of the entropy of the crystal near absolute zero.

This residual anisotropy (due to the Stark-splitting) implies, according to Van Vleck and Penney,[4] a small deviation of the principal susceptibilities of the crystal from the Curie law, the susceptibilities being given by the expressions, of the Weiss type,

$$\chi_1 = \frac{C}{T-\Delta_1}, \chi_2 = \frac{C}{T-\Delta_2}, \chi_3 = \frac{C}{T-\Delta_3}; \quad .. \quad (3)$$

$$\Delta_1 + \Delta_2 + \Delta_3 = 0. \quad .. \quad .. \quad .. \quad .. \quad (4)$$

For manganous ammonium sulphate, taking χ_1 and χ_2 to denote the susceptibilities in the (010) plane, χ_3 that along the '*b*' axis, and χ the mean susceptibility, we find experimentally that, at 30° C.,

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[2] *Naturwiss.*, 1933, **21**, 178.

[3] *Phil. Trans.* (A), 1933, **232**, 99.

[4] *Phil. Mag.*, 1934, **17**, 961.

$$\left.\begin{aligned}\frac{\Delta_1-\Delta_2}{T}&=\frac{\chi_1-\chi_2}{\chi}=\frac{8}{14{,}000}\\ \frac{\Delta_1-\Delta_3}{T}&=\frac{\chi_1-\chi_3}{\chi}=\frac{6}{14{,}000}\end{aligned}\right\}, \quad .. \quad .. \quad .. \quad (5)$$

from which we obtain

$$\Delta_1 = 0{\cdot}10°,\ \Delta_2 = -0{\cdot}07°,\ \Delta_3 = -0{\cdot}03°\ \text{K}. \quad .. \quad (6)$$

Thus the effect of the Stark-splitting on the magnetic behaviour of the crystal is equivalent to that of feeble magnetic fields of the Weiss type.

For temperatures below Δ_1, the corresponding Weiss field may be taken, as usual, to be equal to

$$H_f = \frac{3k\,\Delta_1}{\mu}, \quad .. \quad .. \quad .. \quad .. \quad .. \quad (7)$$

where $\mu = g\beta\sqrt{s(s+1)}$ is the magnetic moment of the ion.

We shall now assume that, just as the influence of the crystalline fields on the magnetic behaviour of the crystal at room temperatures can be treated as being equal to the effect of a certain Weiss magnetic field, the effect of the crystalline fields in orienting the magnetic moments, and thus diminishing the entropy of the crystal at the low temperatures we are considering, would also be equivalent to the effect of the appropriate Weiss field, H_f.

In the adiabatic demagnetization experiment then, just as the entropy under the initial conditions is that of practically free Mn^{++} ions at temperature T_i placed in a magnetic field[5] H_i, the entropy of the crystal at the final temperature T_f under zero external magnetic field would be that of *free* Mn^{++} ions at temperature T_f placed in a magnetic field H_f. Since in the experiment the two entropies should be equal, we obtain

$$\frac{T_f}{T_i}=\frac{H_f}{H_i}=\frac{3k\,\Delta_1}{H_i\,g\beta\sqrt{s\,(s+1)}}, \quad .. \quad .. \quad .. \quad (8)$$

which is very similar to Kürti and Simon's expression [see (1)]

$$\frac{T_f}{T_i}=\frac{k\,\theta_m}{H_i g\beta} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (9)$$

By comparing the two expressions, we obtain for the characteristic temperature of manganous ammonium sulphate[6]

$$\theta_m = \frac{3\Delta_1}{\sqrt{5/2\times 7/2}} = 0{\cdot}10°\ \text{K}\ (0{\cdot}07\ \text{cm.}^{-1}), \quad .. \quad .. \quad (10)$$

which agrees well with Kürti and Simon's value 0·11° K.

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[5] At the initial temperature the influence of the crystalline field on the magnetic entropy would be very small in comparison with that of the applied magnetic field.

[6] The Weiss field H_f for the crystal, at these low temperatures, is found to be about 760 gauss.

Conversely, this agreement may be taken to justify our assumption that the effect of the crystalline field at these low temperatures in orienting the magnetic moments and thus producing a diminution of entropy, is equivalent to the effect of the appropriate Weiss field H_f supposed to act on these moments, which are taken to be otherwise free.

Thus solely from measurements on the magnetic anisotropy of the crystal at room temperatures which can be easily made, it is possible to predict the entropy-temperature curve close to the absolute zero, which (curve) plays an important part in discussions on the production of these low temperatures by adiabatic demagnetization of paramagnetic crystals, and also on their specific heats in this and the neighbouring regions.

THE CARBON ISOTOPE IN RAMAN SCATTERING. PART I.

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Received July 8, 1935.

1. *Introduction.*

Only a few attempts have been made in the past to detect the isotopes of different elements by studying the fine structure of the vibration Raman lines. Amongst these mention may be made of the work of Langseth[1] who found that the principal line shifted by about 455 cm.$^{-1}$ in carbon tetrachloride consists of three close components at 455·07, 458·35 and 461·45 cm.$^{-1}$. He ascribed them respectively to CCl_4^{35}, $CCl_3^{35}Cl^{37}$, $CCl_2^{35}Cl_2^{37}$ molecules and showed that their positions and relative intensities are in qualitative agreement with what may be expected on the basis of such a hypothesis. There appear to be no reliable conclusions regarding the isotopes of other elements. In the Raman spectrum of benzene, various investigators have however recorded some feeble components to the principal 992 line. A simple calculation will show that the satellite at about 984 cm.$^{-1}$ is in the expected position if we regard the same as arising from a benzene molecule in which one of the carbon atoms is replaced by its heavier isotope of atomic weight 13. That such an origin for this line should be regarded as one of the possible alternative explanations was first pointed out by Gerlach.[2] No further information is however available regarding the explanation of the other components. This case will be dealt with more fully in a later section.

A systematic study of the fine structure of the various Raman lines from the point of view of the carbon isotope should be of great help in understanding the nature of the oscillations especially in view of the recent quantitative determinations of the abundance ratio in this case by Aston.[3] For such investigations only lines which are intense, sharp and well polarised* constitute favourable cases and the choice of liquids must naturally be based

[1] A. Langseth, *Z. f. Phys.*, 1931, **72**, 350.
[2] W. Gerlach, *Munch. Ber.*, 1932, Nr. 1, 39.
[3] F. W. Aston, *Proc. Roy. Soc.*, A, 1935, **149**, 396.
* If the line is not well polarised, it develops rotation wings on either side and the separation of weak and closely-spaced satellites becomes much more difficult.

on these considerations. The case of gases will be more favourable as the lines are usually sharp but correspondingly long exposures have to be given even at reasonably high pressures. From a careful consideration of all these points, the following cases have been chosen for investigation, *viz.*, the principal Raman lines in benzene, cyclohexane and cyclopropane liquids and in ethane, ethylene and acetylene gases. The case of diamond is of special interest and may be added to the list. Although the choice has been such that the lines under question are quite sharp and well polarised, it must be mentioned that different separations that are to be expected in the different cases make the use of special types of spectrographs necessary for each one of the cases. In this investigation three different instruments have been used. The present paper describes the results so far obtained by the author in this direction.

Considerable attention is now being devoted to the case of compounds where hydrogen is replaced by deuterium but the problem is evidently of a different type as it does not usually involve a study of the fine structure of the lines.

2. *Experimental Results.*

Benzene.—Specially purified benzene is contained in a suitably painted glass tube and its Raman spectrum is obtained with the help of a Hilger glass littrow spectrograph using a fine slit. With an exposure of about 50 hours, the principal line shifted by 992 cm.$^{-1}$ is recorded with great intensity and a satellite at 985 cm.$^{-1}$ is seen very clearly for both λ 4046 and λ 4358 excitations. A microphotometric record of the principal line and its component excited by λ 4358 is reproduced in the Plate accompanying this paper. Besides the prominent satellite on the low frequency side marked by an arrow, yet another companion which is not very well resolved from the main line, may also be seen on the longer wavelength side. By giving a comparison exposure on the same plate of about 2½ hours, it is found that the intensity of the principal line at 992 cm.$^{-1}$ is about 20 times that of the satellite at 985 cm.$^{-1}$.

Cyclohexane.—Cyclohexane purified by redistillation in vacuum is contained in a suitable glass tube and a Raman spectrum of this substance is obtained with the same instrument. By giving an exposure of 120 hours the principal line at 802 cm.$^{-1}$ is recorded with great intensity and a definite and marked blackening on the shorter wavelength side of this line is noticed. Resolution of this into a separate line could not be effected in this case.

Cyclopropane.—Cyclopropane is condensed from a cylinder into a thick-walled pyrex glass tube using liquid air and when the desired amount is collected, the glass tube is sealed off while under liquid air. In this way,

the liquid is studied under a pressure of about 7 or 8 atmospheres at the room temperature. A Raman spectrum of this substance is obtained using a Fuess glass spectrograph and a fine slit. An exposure of about 72 hours under the most favourable conditions has given an intense Raman spectrum in which the principal line at 1188 cm.$^{-1}$ appears with great intensity. Besides this line, a weak component at 1175 cm.$^{-1}$ whose intensity is about 1/40th of the main line is also recorded. An enlargement of this line excited by λ 4046 is reproduced in the Plate and the component is marked by an arrow. Other interesting features in the Raman spectrum of this substance† that may be noted here are the presence of a definite rotation wing in spite of the relatively low optical anisotropy and a doubling of the band at 1440. Such a doubling is somewhat exceptional in aliphatics and is therefore of special interest. Results of a detailed study of the Raman spectrum of this substance will be reported elsewhere.

Ethane.—Using the high pressure gas tube constructed by the author and described in earlier papers,[4] the Raman spectrum of ethane gas has been photographed with a 2 prism glass spectrograph of high light gathering power giving a continuous exposure of about 20 days. The principal line shifted by 993 cm.$^{-1}$ due to the C—C oscillation is recorded both from λ 4046 and λ 4358 with great intensity. Alongside the principal line but shifted only by 974 cm.$^{-1}$ is recorded another satellite, the intensity of which is roughly 1/40th of that of the main line. An enlargement reproduced in the Plate shows these two lines excited by λ 4358 very clearly. The component to the line excited by λ 4046 may also be seen in the negative. It may be mentioned here that this line has been recorded but not so clearly in an earlier paper by the author[5] where the ethane gas was studied under similar but slightly less favourable conditions.

Ethylene and acetylene have not been studied in the present investigation and the results obtained by the author for diamond in an earlier paper[6] will be quoted here. Working with an exceptionally clear and large piece it has been possible to record a weak line at 1288 along with the principal line at 1332.

The results relevant to the present investigation along with the approximate intensity estimates are given in Table I. The frequencies calculated

† The Raman spectrum of this substance has been studied by R. Lespieau, M. Bourguel and R. Wakemann, *Compt. Rend.*, 1931, **193**, 1087. These authors have reported lines at 1188, 3011 and 3028 and bands at 867, 1439 and 3076.

[4] S. Bhagavantam, *Ind. Jour. Phys.*, 1932, **7**, 107.

[5] S. Bhagavantam, *Ind. Jour. Phys.*, 1931, **6**, 595.

[6] S. Bhagavantam, *Ind. Jour. Phys.*, 1930, **5**, 573.

on the assumption that one of the carbon atoms in each molecule is replaced by its heavier isotope are also given in the Table for comparison.

TABLE I.

Substance	Principal frequency	Satellite frequency (Observed)	Satellite frequency (Calculated)
Benzene	992 (20)	985 (1)	985·7
Cyclohexane ..	802	unresolved blackening	796·7
Cyclopropane ..	1188 (40)	1175 (1)	1172·5
Ethane	993 (40)	974 (1)	973·6
Diamond	1332	1288	1280

3. Comparison of the Results with Existing Observations in Benzene.

The fine structure of the 992 Raman line in benzene has been studied by a number of investigators but as the following table will show, the results due to various investigators are not in satisfactory agreement with each other. The relative intensities of the various components as estimated by the different authors are given in brackets.

TABLE II.

Raman Spectrum of Benzene.

Author	Frequencies and relative intensities						
J. Weiler[7] ..		982 (1)			992·0 (4)		
L. E. Howlett[8] ..	980·3 (5)		983·9 (5)		992·2 (10)	998·8 (5)	10005·3 (0)
P. L. Mesnage[9] ..		981·1 (2)			992·4 (10)		
L. and E. Bloch[10]	978·5 (0)		983·8 (2)	989·1 (?)	992·2 (20)	999 (1)	1006·0 (0)

There are wide discrepancies both as regards the frequencies as well as their relative intensities. Contrary to the above results, in the present investigation only two lines have been observed at 985 cm.$^{-1}$ and 992·2 cm.$^{-1}$ their relative intensities being 1 and 20. In addition to these two, there appears a partially resolved wing on the longer wavelength side of 992·2 cm.$^{-1}$

[7] *Z. f. Phys.*, 1931, **69**, 586.
[8] *Canad. J. Research*, 1931, **5**, 572.
[9] *J. de Phys. et le Rad.*, 1931, **2**, 403.
[10] *Compt. Rend.*, 1933, **196**, 1787.

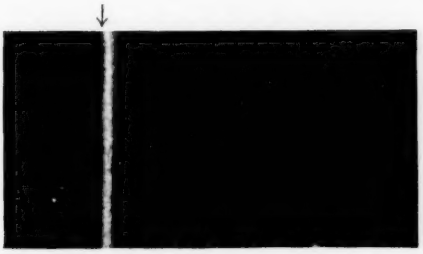
but much closer to it than the line at 985 cm.$^{-1}$. This feature has not been recorded by any of the above observers. The failure to record the other components, *viz.*, 980·3, 999, etc. in the present investigation is very significant. According to the intensity figures given in Table II, it appears that they should have been recorded with the same facility as the one at 985 cm.$^{-1}$ A possible explanation is that they have arisen from traces of impurities such as toluene, etc. in which case we should regard the line at 985 cm.$^{-1}$ as the only genuine companion to the principal line.

4. Discussion of Results.

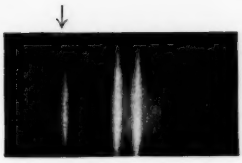
The weak lines obtained in the present investigation, *viz.*, 985 in benzene, 1175 in cyclopropane and 974 in ethane have an important bearing on the problem of isotopes. Taking the principal frequency of benzene as 992·2, it may readily be calculated that the corresponding frequency arising from a benzene molecule in which all the six carbon atoms have the atomic weight 13 should be 953·2. The relative proportion of such molecules will however be very small. On the other hand we may consider the case of the molecule $C_5^{12}C^{13}H_6$ and make an approximate calculation of its frequency by dividing the interval between 992·2 and 953·2 into six parts. We obtain 985·7 as the frequency of this type of molecule in satisfactory agreement with the observed value for the satellite line in benzene. Moreover, the abundance ratio of 140 : 1 recently given by Aston for the carbon isotope C^{13} may be made use of in a very simple way for calculating the relative probabilities of the $C_6^{12}H_6$ and $C_5^{12}C^{13}H_6$ molecules as 23 : 1 which is in very good agreement with the ratio of intensities found for these two lines.

A similar calculation may be made in cyclopropane by assuming the principal frequency to be 1188. The frequency arising from a molecule of the type $C_2^{12}C^{13}H_6$ comes out as 1172·5 in good agreement with the observed value, *viz.*, 1175. The expected intensity ratio is also confirmed experimentally.

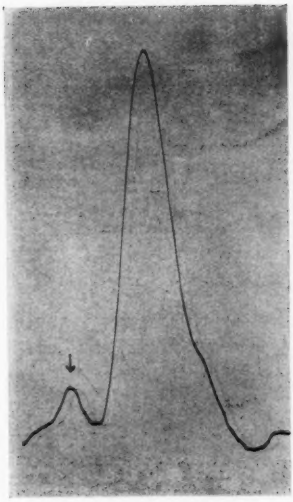
In ethane, the calculation is made by considering the isotopic molecule $C^{12}C^{13}H_6$ as having a reduced mass of $^1/_{12}+^1/_{13}$ instead of $^1/_{12}+^1/_{12}$. Assuming the principal frequency of the oscillation in ordinary ethane as 993, the corresponding frequency in $C^{12}C^{13}H_6$ can be shown to be 973·6 and from the abundance ratio 140 : 1, we should expect the relative populations of these molecules to be in the ratio of 70 : 1. In this case, the calculated frequency 973·6 is in good agreement with the observed one, *viz.*, 974 but the ratio of intensities is not uniquely confirmed. From the photographs it appears that the component accompanying the line excited by λ 4046 has the correct order of intensity whereas the component excited by λ 4358 is a little



(*a*)



(*b*)



(*c*)

(*a*) Cyclopropane. (*b*) Ethane. (*c*) Benzene.

too intense. The possibility of the ethane gas having a higher hydrocarbon impurity which is giving rise to this line has been considered and definitely ruled out as all the higher hydrocarbons have been studied on an earlier occasion by the author and are found to exhibit no strong lines having a frequency near enough to 974. On the other hand there is a certain chance of a weak hydrogen oscillation having a low frequency such as 2740, hitherto undetected in ethane being present but it appears most unlikely that the coincidence can be so exact.

In the case of diamond also, the agreement between the observed and calculated values may be considered satisfactory in view of the large shift and the feebleness of the line in question. The cases of ethylene and acetylene are being studied and the results will be reported in due course.

5. *Summary.*

The principal Raman lines in benzene, cyclopropane and ethane shifted by 992, 1188 and 993 wave numbers respectively are found to have feeble companion lines of frequency shifts 985, 1175 and 974. These are attributed to molecules in which one of the carbon atoms is replaced by its heavier isotope C^{13}, *viz.*, $C_5^{12}C^{13}H_6$, $C_2^{12}C^{13}H_6$ and $C^{12}C^{13}H_6$ respectively. The positions and the relative intensities agree satisfactorily with this view.

In conclusion, the author desires to express his grateful thanks to Prof. Sir C. V. Raman for his kind interest in the work.

A SUGGESTED NEW INTERPRETATION OF THE STRUCTURE OF BAND-SPECTRA.

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*1. Introduction.**

It is well known that in general an electronic band of the simplest type due either to the emission or absorption by a diatomic molecule can be regarded as consisting of a series of lines all of which can be represented, to a first approximation, by a formula of the type $\nu = \nu_0 + BM + CM^2$, where M assumes in succession the values ± 1, ± 2, ± 3, ... etc. In the above formula $C = \frac{h}{8\pi^2 CI'} - \frac{h}{8\pi^2 CI''}$ where I′ and I″ refer to the two electronic states causing the band in question. It is easily shown that such a formula gives rise to two different types of bands according as the constant C is positive ($I' < I''$) or negative ($I' > I''$). In the former case the band appears *degraded towards the violet* whereas in the latter it appears *degraded towards the red.* These general characters persist even in complicated types of bands and imply that absorption of energy by molecules can in some cases (*band degraded towards the violet*) result in a diminution of the equilibrium distance between the nuclei whereas in some others (*band degraded towards the red*) it can result in an increase. Closely connected with the change in the equilibrium nuclear distance of a molecule on being raised to a higher electronic state is the well-known fact that the binding strength between the two nuclei

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* The notation employed in this paper is as follows:—

h	= Planck's constant.
c	= Velocity of light.
U	= Potential energy of the molecule.
μ	= Reduced mass; $x_e w_e$ = Anharmonic constant.
ν_e	= Spacing of the two electronic levels involved.
μ_1, μ_2	= Electric moments induced in each of the two atoms.
I′, I″	= Moments of inertia in the upper and lower electronic states respectively.
r_e', r_e''	= Equilibrium distances between the nuclei for the upper and lower electronic states respectively.
w_e', w_e''	= Vibration frequencies for the upper and lower electronic states respectively.

and with it the vibrational frequency also undergo marked changes. As is well known there is a striking relationship between the two phenomena ; if on being raised to a higher electronic state, the equilibrium distance between the nuclei of a molecule increases, the vibrational frequency is diminished, whereas if the equilibrium distance between the nuclei diminishes, the vibrational frequency is increased. These statements, to which there are only a few minor exceptions, are solely based on experimental facts and are to a large extent empirical. The existing ideas relating to the mechanism of light absorption by molecules provide no clue whatsoever as to either the direction or magnitude of the changes in the nuclear distances and the vibration frequencies to be expected when a molecule absorbs energy and passes over into a higher electronic state. It is the purpose of the present paper to suggest a new line of thought in this direction, which it is hoped will form the basis of a satisfactory interpretation of the experimental facts.

2. The Potential Energy Function and Molecular Properties.

Several equations[1,2,3] have been proposed which express the potential energy due to nuclear motion of a diatomic molecule as a function of the nuclear distance. These equations which are of fundamental significance in connection with problems relating to molecule formation involve constants such as the equilibrium nuclear distance, the vibration frequency and the anharmonic correction characterising the molecule in each one of its electronic states. It is possible to evaluate the potential energy function for the different electronic states of a molecule if the constants that enter into the equations are known and these constants (r_e, w_e and $x_e w_e$) for the different states of the molecule can at present be determined only experimentally if the band spectrum is completely analysed. Further, a theoretical computation and hence a prediction of the molecular properties in the different electronic states should also be possible. Mathematical difficulties have however prevented such calculations being successfully made except for two very simple cases of diatomic molecules, *viz.*, the hydrogen molecular ion and the hydrogen molecule, the potential energy curves for the various electronic states of which have been computed by Burrau, Morse and Stueckelberg, Heitler and London and others using different wave mechanical methods. No calculations of this type however are available for more complex systems.

From a study of the data available in a large number of cases, certain empirical rules have however been given which endeavour to correlate the

[1] Fues, *Ann. der Phys.*, 1926, **80**, 367.

[2] Morse, *Phys. Rev.*, 1929, **34**, 57.

[3] Rydberg, *Z. f. Phys.*, 1931, **73**, 376.

different equilibrium nuclear distances and the vibration frequencies of a molecule in its various electronic states. Amongst these mention may be made here of the following due respectively to Mecke[4], Morse[5] and Badger[6]. $w_e r_e^2 = \text{Constant}$ .. (1) ; $w_e r_e^3 = \text{Constant}$ .. (2) ; $k_0(r_e - d)^3 = \text{Constant}$ .. (3) Equation (1) applies to the different electronic states of a given molecule, equation (2) applies to the different electronic states not only of a given molecule but also of a group of different molecules and equation (3) applies to all molecules with varying values for d.

3. *Theory of Induced Electric Doublets.*

We shall now proceed to consider the mechanism of light absorption by a diatomic molecule. It will be assumed that the light wave, in the first instance, only affects the motion of the extra nuclear electrons. From an analogy with the classical theory of optical polarisation, we may regard the atoms as centres of temporary electrical doublets formed under the influence of the electric field in the incident light wave and all changes in the nuclear constants which occur when the molecule passes over into a higher electronic state are regarded as consequential on the formation of such electric doublets. As has already been remarked, there are two types of transitions one in which the equilibrium nuclear distance increases and the other in which it diminishes by light absorption. Various possibilities arise regarding the direction of the axes of the two doublets in the molecules, both with reference to one another, and with reference to the nuclear axis. For simplicity[5] we make what appears to be the most reasonable assumption, namely, that they are parallel to each other and lie either along the nuclear axis or transverse to it. In the former case, the doublets attract each other with a force equal to $\frac{6\mu_1\mu_2}{r^4}$ and in the latter case repel each other with a force equal to $\frac{3\mu_1\mu_2}{r^4}$ where μ_1 and μ_2 are the electric moments acquired by each of the two atoms. μ_1 and μ_2 will be regarded as equal to one another if the two atoms are identical. Under these conditions a new equilibrium will be established and the equilibrium distance will be less or more than the initial value according as the doublets are of the former or of the latter type. If we take the initial potential energy curve to be represented by the well-known Morse function, the potential energy after formation of the above doublets may respectively be written in the two cases as

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[4] *Z. f. Phys.*, 1925, **32**, 823.

[5] *Phys. Rev.*, 1929, **34**, 57.

[6] *Jour. Chem. Phys.*

$$U_r = -2De^{-a(r-r_e)} + De^{-2a(r-r_e)} - \frac{2\mu_1\mu_2}{r^3} \quad .. \quad .. \quad (1)$$

$$U_r = -2De^{-a(r-r_e)} + De^{-2a(r-r_e)} + \frac{\mu_1\mu_2}{r^3} \quad .. \quad .. \quad (2)$$

In these equations $D = \frac{w_e^2 hc}{4x_e w_e}$ and $a = \sqrt{8\pi^2 c\, x_e w_e \mu/h}$ and the various letters have the usual significance.* Equations (1) and (2) may be expanded and rewritten as (3) and (4) respectively after neglecting higher powers.

$$U_r = -D + a^2(r-r_e)^2 D \ldots . - \frac{2\mu_1\mu_2}{r_e^3}\left[1 - \frac{3(r-r_e)}{r_e} \ldots .\right] .. \quad (3)$$

$$U_r = -D + a^2(r-r_e)^2 D \ldots . + \frac{\mu_1\mu_2}{r_e^3}\left[1 - \frac{3(r-r_e)}{r_e} \ldots .\right] .. \quad (4)$$

In order to obtain the conditions for the new equilibrium positions, we differentiate (3) and (4) and equate the forces to zero and derive the following relations.

$$(r_e - r) = \frac{3\mu_1\mu_2}{r_e^4 a^2 D} \quad .. \quad (5) \qquad (r - r_e) = \frac{3\mu_1\mu_2}{2r_e^4 a^2 D} \quad .. \quad (6)$$

In these equations $a^2 D = 2\pi^2 c^2 w_e^2 \mu$. Equations (5) and (6) correspond respectively to the cases of attraction and repulsion. In the former, the final equilibrium value of the nuclear distance is less than the initial value r_e and *vice versa* in the latter. The value of $\mu_1\mu_2$ pertaining to an electronic transition in any one molecule, which represents the strength of the induced doublets that have to be postulated to account for the observed changes in the equilibrium nuclear distances, may be obtained by substituting the actual changes derived from the absorption spectrum data in equations (5) and (6). The electric moments for a large number of molecules calculated in this manner are contained in the eleventh column of Tables I and II.

If $\frac{\mu_1\mu_2}{r^3}$ *is small in comparison with D*, the important terms in equations (3) and (4) may be rewritten as

$$-D - \frac{2\mu_1\mu_2}{r_e^3} - \frac{9\mu_1^2\mu_2^2}{r_e^8 a^2 D} + a^2\left(D + \frac{2\mu_1\mu_2}{r_e^3} + \frac{9\mu_1\mu_2}{r_e^8 a^2 D}\right)\left(r - r_e + \frac{3\mu_1\mu_2}{r_e^4 a^2 D}\right)^2 \quad .. \quad (7)$$

$$-D + \frac{\mu_1\mu_2}{r_e^3} - \frac{9\mu_1^2\mu_2^2}{4r_e^8 a^2 D} + a^2\left(D - \frac{\mu_1\mu_2}{r_e^3} + \frac{9\mu_1\mu_2}{4r_e^8 a^2 D}\right)\left(r - r_e - \frac{3\mu_1\mu_2}{2r_e^4 a^2 D}\right)^2 \quad .. \quad (8)$$

* See Condon and Morse, *Quantum Mechanics*, page 163.

TABLE I.

Bands Degraded to the Violet.

Molecule	ν_e cm.$^{-1}$	r_e'' A.U.	r_e' A.U.	w_e'' cm.$^{-1}$	$x_e''w_e''$ cm.$^{-1}$	$D_e'' \times 10^{11}$	$D_e' \times 10^{11}$ (calc.)	w_e' (calc.)	w_e' (obs.)	$\sqrt{\mu_1\mu_2} \times 10^{18}$ calc. Band spectra	$\sqrt{\mu_1\mu_2} \times 10^{18}$ calc. polarisability
BeH	20031	1·340	1·330	2058·5	35·50	0·586	0·596	2076	2088	0·348	..
CaH	14432	2·020	1·990	1316·7	19·20	0·443	0·464	1347	1333	0·911	..
CN	25798	1·169	1·148	2068·8	13·18	1·594	1·730	2155	2164	1·029	2·245
MgH	19271	1·730	1·680	1493·5	31·25	0·350	0·388	1572	1604	0·971	..
C_2	19379	1·308	1·261	1641·6	11·67	1·133	1·337	1783	1793	1·472	2·122
N_2^+	25566	1·113	1·071	2206·8	16·04	1·490	1·819	2438	2418	1·463	2·076
B'O	19344	1·348	1·301	1259·1	10·60	0·734	0·869	1370	1280	1·251	..
N_2	29653	1·201	1·140	1732·8	14·44	1·021	1·344	1988	2045	1·613	2·236
NO	44193	1·146	1·060	1906·5	14·42	1·237	1·815	2310	2375	1·977	2·747
CO	22164	1·232	1·118	1516·7	17·24	0·655	1·145	2005	2182	2·005	2·021

These may again respectively be regarded as the first two terms of modified Morse functions (9) and (10).*

$$-2D'e^{-a(r-r_e')} + D'e^{-2a(r-r_e')} \quad .. \quad .. \quad .. \quad .. \quad (9)$$

$$-2D'e^{-a(r-r_e')} + D'e^{-2a(r-r_e')} \quad .. \quad .. \quad .. \quad .. \quad (10)$$

Equation (9) signifies that the creation of two attracting doublets of strength μ_1 and μ_2 may be regarded to a first approximation as causing an increase of the dissociation energy to D' equal to $D + \frac{2\mu_1\mu_2}{r_e^3} + \frac{9\mu_1^2\mu_2^2}{r_e^8 a^2 D}$ with a corresponding diminution of the equilibrium nuclear distance to r_e' equal to $r_e - \frac{3\mu_1\mu_2}{r_e^4 a^2 D}$. Similarly equation (10) signifies that two repelling doublets μ_1 and μ_2 cause a diminution of the dissociation energy to D' equal to $D - \frac{\mu_1\mu_2}{r_e^3} + \frac{9\mu_1^2\mu_2^2}{4r_e^8 a^2 D}$ with a corresponding increase in the equilibrium nuclear distance to r_e' equal to $r_e + \frac{3\mu_1\mu_2}{2r_e^4 a^2 D}$. In both cases D is equal to

* This mode of representation is exactly similar to the one adopted in studying the effect of adding a small kinetic energy term due to the rotation of a molecule to its nuclear potential energy. For the details of calculation see Condon and Morse, *Quantum Mechanics*, page 164.

TABLE II.

Bands Degraded to the Red.

Molecule	ν_e cm.$^{-1}$	r_e'' A.U.	r_e' A.U.	w_e'' cm.$^{-1}$	$x_e''w_e''$	$D_e'' \times 10^{12}$	$D_e' \times 10^{12}$ (calc.)	w_e' (calc.)	w_e' (obs.)	$\sqrt{\mu_1\mu_2} \times 10^{18}$ calc. Band spectra	$\sqrt{\mu_1\mu_2} \times 10^{18}$ calc. polarisability
AgH	29898	1·614	1·638	**1760·0**	34·05	4·465	4·237	**1714**	**1664**	0·991	..
O_2	13121	1·204	1·223	**1568·0**	11·65	10·350	9·493	**1502**	**1433**	1·237	1·415
BeF	33187	1·357	1·390	**1265·6**	9·12	8·612	7·790	**1190**	**1173**	1·460	..
BeO	21197	1·328	1·359	**1487·5**	11·87	9·154	8·166	**1406**	**1371**	1·549	..
AlO	20635	1·614	1·663	**977·0**	7·00	6·692	5·280	**868**	**868**	2·493	..
CuH	23311	1·460	1·568	**1939·9**	36·85	5·013	3·992	**1731**	**1700**	1·891	..
Li_2	20395	2·670	2·930	**351·6**	2·59	2·342	1·842	**312**	**270**	3·339	..
CO^+	45638	1·110	1·160	**2212·0**	15·17	15·830	12·440	**1962**	**1722**	2·229	2·900
HgH^+	44108	1·590	1·690	**2016·0**	40·80	4·889	3·744	**1764**	**1647**	2·254	..
CN	10900	1·169	1·236	**2068·8**	13·18	15·930	12·060	**1800**	**1789**	2·599	1·459
Na_2	20302	3·070	3·404	**159·2**	0·73	1·714	1·226	**135**	**124**	4·106	..
K_2	15369	3·910	4·220	**92·6**	0·35	1·190	0·841	**78**	**75**	4·863	..
AuH	27345	1·520	1·670	**2302·0**	42·00	6·193	4·181	**1891**	**1690**	2·879	..
ZnH^+	46432	1·510	1·710	**1916·0**	39·00	4·619	2·899	**1518**	**1365**	2·719	..
CdH^+	42680	1·660	1·860	**1773·0**	36·50	4·227	2·562	**1380**	**1250**	3·049	..
S_2	31673	1·603	1·806	**727·4**	2·75	9·441	5·080	**534**	**435**	4·709	4·306
PbO	30106	1·918	2·042	**722·3**	3·73	6·864	3·621	**525**	**531**	5·032	..
MgH^+	35629	1·649	2·008	**1702·2**	34·20	4·157	1·979	**1174**	**1138**	3·808	..
P_2	46802	1·880	2·120	**779·3**	2·72	10·960	4·258	**486**	**471**	7·423	..
SO	39109	1·489	1·769	**1123·7**	6·12	10·140	2·271	**532**	**629**	6·017	3·078

$\frac{hcw_e^2}{4x_ew_e}$ and as it is assumed that a and hence x_ew_e does not change, the new value of w_e the vibration frequency, may easily be calculated. It may, however, be remarked even here that it follows very naturally from the equations that an increase in the equilibrium nuclear distance is always accompanied by a diminution of the vibration frequency and *vice versa*. This conclusion is in entire agreement with the observed facts.

4. Comparison of Theory and Experiment.

The theory outlined in the foregoing section has been applied to almost all cases of bands for which complete data are available. The data contained in Tables I and II are taken from the International Critical Tables, Vol. 5, and "Report on Band Spectra of Diatomic Molecules" by W. Jevons. Unit of ν_e, w_e'' and w_e' is one cm.$^{-1}$ and of r_e'' and r_e' is 10^{-8} cm.

5. An Independent Method of Calculating the Electric Moments.

An alternative method is to regard the energy of electronic excitation as having been spent in creating an electric moment in the molecule. If it is assumed that the molecule is composed of uniformly polarisable matter of volume v, having a dielectric constant K and an optical polarisability P the energy of electrification is easily seen to be $\frac{E^2(K-1)v}{8\pi}$ where E represents the field strength. This may be rewritten as $\frac{E^2P^2v^2}{2Pv}$ after multiplying both the numerator and denominator by Pv since $K - 1 = 4\pi P$. The numerator represents the square of the total moment $\bar{\mu}$ induced in the molecule as a result of electronic excitation and the denominator is twice the polarisability $\bar{P}$ per single molecule. Equating this to the energy of electronic excitation we have

$$\frac{\bar{\mu}^2}{2\bar{P}} = h\nu c \text{ or } \bar{\mu}^2 = 2\,\bar{P}\,h\nu c$$

for a transition in which ν represents the spacing of the two electronic levels involved. $\bar{P}$ is the polarisability of the molecule in question and if it is known, the value of $\bar{\mu}$ may be calculated. In case of molecules having identical atoms, it is assumed that this moment is shared equally by them and in other cases, it is divided in the ratio of the optical polarisabilities of the constituent atoms, thus obtaining the values of μ_1 and μ_2 of the preceding section which together constitute $\bar{\mu}$ the total moment of the molecule. The quantity $\sqrt{\mu_1\,\mu_2}$ calculated in this way for a few molecules for which data are available is given in the last column of Tables I and II which may be compared with a similar quantity in the adjoining column.

6. Discussion of Results.

The outstanding feature exhibited by the results in the eleventh column of Tables I and II is the close correspondence between their order of magnitude and the permanent electric moments that are frequently met with in molecules. This lends a strong support to the ideas contained in the present paper. The frequency in the lower state and the frequencies (calculated and observed) in the upper state have been printed in thick type to facilitate comparison.

In Table I, the agreement between the calculated and observed values is very satisfactory in practically all the cases studied. In Table II, in most cases, the agreement is satisfactory but there are some which are marked by unsatisfactory agreement (CO^+, AuH, ZnH, etc.). These remarks have to be considered along with the following facts. For some reason, the changes in the nuclear distance are usually small and the term $\frac{2\mu_1\mu_2}{r^3}$ or $(D_e'' - D_e')$ is also small in comparison with D_e'' in the case of bands degraded to the violet and we are therefore justified in regarding $\frac{2\mu_1\mu_2}{r^3}$ as a perturbing energy and the results consequently are universally satisfactory. On the other hand, in the case of bands degraded to the red, the changes in the nuclear distance are large and $(D_e'' - D_e')$) is in many cases comparable to D_e'' (AuH downwards in Table II) and in such cases we cannot expect the method to work at all. Nevertheless it is remarkable how the large changes, as for instance in the case of SO and P_2, are indicated correctly but it must be pointed out that good agreement in such cases may partly be accidental. In the case of halogens (Cl_2, Br_2 and I_2) the term $\frac{\mu_1\mu_2}{r^3}$ becomes very large as the atoms are very heavy and the changes in the nuclear distances are appreciable and the method totally fails as may be expected. These are therefore not included in the Tables.

Another remarkable feature which lends support to the foregoing ideas is the general correspondence between the values of electric moments given in the last two columns of Tables I and II in spite of the fact that the methods by which they have been derived are entirely independent. Even more interesting is the result that large electric moments have to be postulated in order to account for the observed changes in the nuclear distances of highly polarisable substances like Na_2, K_2, S_2 and P_2. This indicates an unmistakable relationship between the phenomenon of optical polarisability and the mechanism of electronic excitation which forms the starting point of the present paper.

7. *Summary.*

The process of electronic excitation of molecules is pictured in the following way. It is assumed that under the action of the incident light wave, the atoms become electric doublets whose axes can be either both parallel or both perpendicular to the nuclear axis. In the former case, the doublets attract each other and the equilibrium nuclear distance diminishes on electronic excitation. In the latter, they repel each other and the equilibrium nuclear distance increases. Both these types of transitions are known to exist. From the observed changes in the nuclear distances, a calculation is

made of the electric moments that are to be postulated in several cases and it is found that these are of the same order of magnitude as the permanent moments frequently met with in molecules.

By adding the mutual potential energy of the doublets to the nuclear potential energy function, it is shown that the creation of doublets may be regarded as equivalent to an increase in the vibrational frequency of the molecule if they are of an attracting type and a decrease of the vibrational frequency if they are of a repelling type. This explains in a very satisfactory manner the well-known experimental fact that increase in the nuclear distance on electronic excitation is always accompanied by a diminution in the vibrational frequency and *vice versa*. Quantitative calculations reveal good agreement between the theoretically deduced and the experimentally observed oscillation frequencies in the higher electronic states for molecules in which changes of nuclear distances are relatively small.

An independent method of calculating the strength of the induced electric moments is given by assuming that the energy of electronic excitation is all spent in polarising the atoms. Good agreement is observed between the values so calculated and the moments deduced from the known changes in the nuclear distances. It is found that large electric moments have to be postulated to account for the observed changes in the nuclear distances and vibration frequencies of highly polarisable molecules, thus indicating a fundamental relationship between the phenomenon of optical polarisability and electronic excitation.

In conclusion the author desires to express his grateful thanks to Prof. Sir C.V. Raman for many helpful discussions during the progress of this work.

ISOTOPE ABUNDANCE IN PLATINUM.

By B. Venkatesachar
and
L. Sibaiya,
(*Department of Physics, University of Mysore, Bangalore.*)

Received July 5, 1935.

In our previous investigation* to deduce the isotopic constitution of platinum from a hyperfine-structure study of its arc lines, we have concluded that platinum contains, in decreasing order of abundance, the isotopes 196, 195, 194 and 192. From eye-estimates of the intensities of the components of λ 3408·13 Å and λ 3042·63 Å, the relative abundance of the isotopes was estimated. Due to the difficulties inherent in a visual estimate of the relative intensities, the actual evaluation of the correct relative abundance had to wait till the microphotograms of the structure pattern of λ 3408·13 Å were obtained.

The necessary microphotographs have now been obtained with a Cambridge Recording Microphotometer. Light transmitted through the structure pattern is incident on a slit over a standard Osram photoelectric cell. The potential developed across a second cell (used as a Koch resistance) by the passage of the photoelectric current is measured by a Lindemann electrometer, the image of whose needle is projected on to a revolving drum camera carrying a bromide paper. As the plate is moved forward synchronously with the rotation of the drum, the density changes of the plate are automatically recorded on the photographic paper. In Plate III, two microphotographs of the same order in the structure pattern of λ 3408·13 Å are reproduced. Fig. 1 is obtained with a slit width of 5/600 mm.; the components are well separated, but the narrow slit brings out the grains in the background. Fig. 2 is taken with a slit width of 8/600 mm.; the three central components are merged together, while the background effect is not prominent. Many more curves were also obtained and the intensity estimates were conducted in two ways. Firstly, the component intensities were so adjusted and their contours were so sketched as to give the observed resultant curve here reproduced; the extreme components due to Pt 195 were assumed to have the theoretical ratio of intensities, *viz.*, 10 : 8. This

* Venkatesachar and Sibaiya, *Proc. Ind. Acad. Sci.*, 1935, **1**, 955–960.

result arises out of the fact that the upper level $5d^6 6s6p\ z^5D_4^\circ$ is considered to be unsplit, while to the lower level $5d^6 6s^2 a^3F_4$ is attributed a separation of 0·475 cm.$^{-1}$ The nuclear spin of Pt 195 being $\frac{1}{2}\frac{h}{2\pi}$, the fine quantum numbers of the level a^3F_4 are 9/2 and 7/2. The intensities of the components being proportional to the quantum weights $(2f+1)$, it follows that the ratio of the intensities of the components is 10 : 8. In the second method the microphotometer curve was obtained over three consecutive orders; the peaks of corresponding components were joined by smooth curves all of which ran nearly parallel to each other. The intensities were estimated with the same assumption as before.

The average value for the relative abundance of the isotopes obtained from more than three determinations in each method is as follows :—

Mass Number ..	196	195	194	192
Relative Abundance ..	16	13	10	~2

The order of abundance is consistent with the one given earlier by visual estimates of intensities. The calculation of the atomic weight from the above relative abundance of the isotopes gives a value which is nearer 195·0 than 195·2. The existence of heavier isotopes, especially Pt 198, in smaller abundance may account for this difference. But with the present data the chemical atomic weight must be considered to be somewhat high.

We desire to express our grateful thanks to Dr. Royds who has kindly taken microphotograms of the original negative on the Cambridge Microphotometer of the Kodaikanal Observatory.

Note added in proof :—

While the paper was in press two letters regarding the isotopes of platinum have come to our notice. Fuchs and Kopfermann (*Naturwiss.*, 1935, **23,** 372) have concluded by hyperfine structure analysis that platinum consists of three isotopes 196(8), 195(8) and 194(5); their results are in general agreement with our previous conclusions (*Proc. Ind. Acad. Sci.*, 1935, **1**, 955–960), except for the fact that they have not obtained any evidence for the existence of platinum isotope 192. Their estimate of the relative abundance of Pt 196 and Pt 194 agrees with ours and shows by inference a positive isotope shift in platinum. More recently a letter by Dempster has appeared in *Nature* (1935, **135**, 993); using a spark discharge between platinum electrodes and a new type of mass-spectrograph, he finds in platinum the isotopes 196, 195 and 194 with nearly equal abundance, while the decidedly less abundant 198 is considerably more abundant than 192. This would require that the faintest component in our pattern (−0·176 cm.$^{-1}$ of λ 3408·13 Å) has to be attributed to 198 instead of 192,

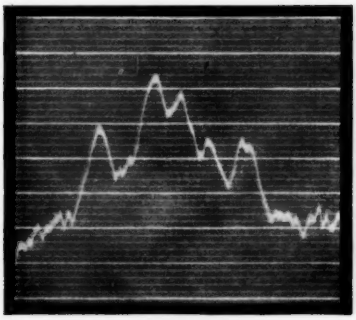

FIG. 1.

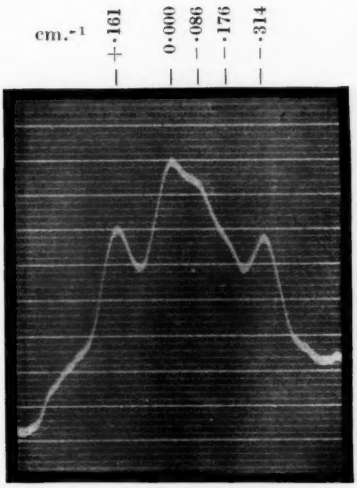

FIG. 2.

Microphotograms of the Structure Pattern of PtI λ 3408·13Å.

UNIV. OF MICH.

thus leading to a negative isotope shift. The relative abundance of the isotopes would then be as follows :—

Mass Number	..	194	195	196	198
Relative abundance	..	16	13	10	~2

This distribution of isotopes gives again a value for the atomic weight near 195·0. The isotopes of platinum in decreasing order of abundance will be 194(16), 195(13), 196(10) and 198(~2) instead of 196(16), 195(13), 194(10) and 192(~2) ; there can be no doubt that isotopes 196 and 194 are markedly unequal in abundance. Mention must however be made of the fact that if the new interpretation is accepted it leads to the rather unusual result that the centre of gravity of Pt 195 lies nearer to Pt 196 than to Pt 194. In all known cases the centre of gravity of the hyperfine structure components due to an odd isotope falls nearer the even isotope of lower mass number. Before a final decision is reached as to which of the two above interpretations has to be accepted, one has to wait till the details of Dempster's investigation are published.

Summary.

The relative abundance of the isotopes of platinum is estimated from an analysis of the microphotograms of the structure pattern of Pt I λ 3408·13 Å ($a^3F_4 - z^5D_4^\circ$). Assuming a positive isotope shift, the isotopes of platinum with their relative abundance are as follows :—

Mass Number	..	196	195	194	192
Relative abundance	..	16	13	10	~2

Dempster's recent letter to *Nature* however suggests a negative shift and the added note gives, in decreasing order of abundance, the isotopes 194(16), 195(13), 196(10) and 198(~2). This interpretation is not consistent with the usual observation that the centre of gravity of an odd isotope lies nearer to the lighter even isotope. The computed atomic weight in either case lies in the neighbourhood of 195·0. Other isotopes in small abundance may account for the divergence between the computed atomic weight and the chemical atomic weight.

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RAMAN SPECTRA OF ISOPRENE, DIPENTENE AND OCIMENE.

By P. S. Srinivasan.
(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received June 18, 1935.
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Experimental.

The present investigation was undertaken as part of a scheme for the investigation of the nature and physical properties of rubber. As is well known, rubber is a high-molecular weight polymer of isoprene and as a preliminary it was thought worthwhile to study the Raman effect in isoprene (C_5H_8), dipentene ($C_{10}H_{16}$) and ocimene ($C_{10}H_{16}$) of which isoprene alone has already been studied by Dadieu and Kohlrausch[1] while the other two which are its isomeric polymers have been studied now for the first time.

All the compounds being liquids, the well-known method of obtaining the Raman spectrum by focussing the image of a mercury arc into the liquid contained in a Wood's tube by means of a condensing lens and then focussing the transversely scattered light on to the slit of a spectrograph, was used. The liquids were all distilled in vacuo a number of times to render them dust-free.

A Hilger two-prism spectrograph was used in the case of isoprene while a slightly higher dispersion Feuss spectrograph was used in the case of the other two liquids. Throughout hypersensitive panchromatic plates were employed. For determining the wave-length a comparison iron arc was taken on each plate and the lines were measured by interpolation.

Of the substances employed, isoprene was prepared chemically pure by the author according to the method described by Basset and Williams.[2] Pale crepe rubber cut into pieces of about 1 gm. each was dropped into a specially constructed iron retort maintained electrically at 600°C., one piece at a time and the products of cracking were collected in two systems of condensers, one maintained at 50°C. and the other in ice and salt. The product collected in the cold condensers was fractionated a number of times and the fraction boiling steadily at 32°·5 C. (680 mm.) was collected.

[1] Dadieu and Kohlrausch, *Ber. Deut. Chem. Gess.*, 1930, **63** (3), 1657.

[2] Basset and Williams, *J. C. S.*, 1932, p. 2324.

The dipentene used in the experiment was a sample obtained as pure from E. de Haen and it was further purified by two distillations under reduced pressure over sodium.

The ocimene was prepared in a very pure state and lent to the author for this work by Mr. B. Sanjiva Rao of the Organic Chemistry Department of the Institute and the author wishes to take this opportunity of thanking Mr. Sanjiva Rao for his kindness.

2. Results.

In the following tables the various exciting lines of the mercury arc are designated by the letters of the alphabet; thus *a*, *b*, *c*, *d*, *e*, *f*, *g*, *h*, *j*, *k* and *l* stand respectively for 3650·3, 3654·9, 3663·3, 3984·1, 4046·8, 4078·1, 4339·5, 4347·7, 4358·6, 4916·4 and 5461.

The numerical subscripts attached to the several letters indicate the relative intensities of the Raman lines excited by the corresponding mercury line on an arbitrary scale wherein the intensity of the Rayleigh scattered 4916 line is taken as 10.

Table I gives the Raman frequencies of isoprene.

TABLE I.

$CH_2=C(CH_3)-CH=CH_2$ *Isoprene.*

No.	Shift ν cm.$^{-1}$	Exciting lines with intensity	No.	Shift ν cm.$^{-1}$	Exciting lines with intensity
1	525·4	$e_1 j_4$	8	1382·3	h_1 (?)
2	778	j_2	9	1422·4	$e_3 j_3$
3	899·8	$e_2 j_2$	10	1636·8	j_{10}
4	950·8	$e_1 j_1$	11	2914·3	e_3
5	994·1	$e_1 j_1$	12	2981·2	b_2
6	1066·6	$e_3 j_4$	13	3015·7	$e_5 j_4$
7	1292·5	$e_5 j_5$	14	3092	e_2

Table II gives a comparison of the frequency shifts obtained by the author with those obtained by Dadieu and Kohlrausch, the figures in the brackets indicating the intensities of the respective Raman lines. Of the two low frequencies 289 and 423 reported by Dadieu and Kohlrausch and

not appearing in the present work, the former is considered uncertain even by Dadieu and Kohlrausch themselves. The agreement otherwise is good.

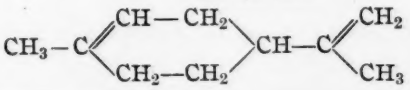
TABLE II.

Comparison Table for Isoprene.

No.	Author	Dadieu and Kohlrausch	No.	Author	Dadieu and Kohlrausch
1	....	289 (1) (?)	9	1292·5 (5)	1291 (5)
2	....	423 (2)	10	1382·3 (1)	1380 (1)
3	525.4 (4)	530 (4)	11	1422·4 (3)	1420 (5)
4	778 (2)	779 (2)	12	1636·8 (10)	1636 (10)
5	899·8 (2)	899 (3)	13	2914·3 (3)	2920 (2)
6	950·8 (1)	954 (4)	14	2981·2 (2)	2983 (1)
7	994·1 (1)	994 (2)	15	3015·7 (5)	3010 (5)
8	1066·6 (4)	1070 (4)	16	3092 (2)	3083 (3)

Table III gives the results for dipentene using the same notation as before.

TABLE III.

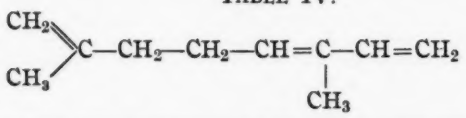


Dipentene.

No.	Shift ν cm.$^{-1}$	Exciting lines with intensities	No.	Shift ν cm.$^{-1}$	Exciting lines with intensities
1	635·7	$e_1 j_{0\cdot5}$	9	1306·9	$e_1 j_2$
2	673·7	$e_1 j_{0\cdot5}$	10	1375	$e_1 j_2$
3	713·7	$e_1 j_{0\cdot5}$	11	1440·2	$e_1 j_2$
4	760·1	$e_2 j_3$	12	1610·6	$e_3 j_6 g_1 h_1$
5	818·5	$e_1 j_{0\cdot5}$	13	1673 (broad)	j_1
6	879·2	$e_2 j_3$	14	2868·5	$e_3 j_2$
7	1051·5 (band)	$j_{0\cdot5}$	15	2922	$e_3 j_2$
8	1207·3	$e_1 j_3$	16	2971·5	$e_3 j_2$

The various frequency shifts obtained with ocimene are given in Table IV.

TABLE IV.



Ocimene.

No.	Shift ν cm.$^{-1}$	Exciting lines with intensities	No.	Shift ν cm.$^{-1}$	Exciting lines with intensities
1	433	$e_1 j_1$	9	1376·6	$e_1 j_1$
2	752·8	$e_{0\cdot5} j_{0\cdot5}$	10	1406·1	$e_3 j_2$
3	885·4	$e_1 j_1 g_{0\cdot5} h_{0\cdot5}$	11	1440	$j_1 d_{0\cdot5}$
4	959·1	$e_1 j_2$	12	1634	$e_4 j_7 g_5 h_1$
5	1069·5	$e_1 j_1$	13	1666	j_3
6	1235·3	$e_2 j_3$	14	2912	$e_3 j_1$
7	1285·3 (band)	$e_2 j_1$	15	2983	j_1
8	1344·4	$e_1 j_{0\cdot5}$	16	3055	$e_1 j_1$

3. *Discussion.*

(*a*) *Relation to Chemical Constitution.*

Isoprene is represented by the formula C_5H_8 and it has therefore 33 degrees of freedom which should all be represented in the Raman spectrum. Some of these might be forbidden and some others might be duplicated so that all the 33 frequencies cannot be reasonably expected. It is however remarkable that only 14 frequencies have been observed by the author while Dadieu and Kohlrausch have observed only one more.

It is well known that the frequency of oscillation of two atoms or groups of atoms can be calculated from a knowledge of the binding force between them and their masses by means of the formula

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}}$$

or from the heat of dissociation of the respective groups from the formula

$$\nu = K\sqrt{\frac{A}{\mu}}$$

where ν represents the frequency of oscillation ;

f represents the binding force ;

μ represents the reduced mass;

A represents the energy of dissociation;

and K is a constant equal to 291·5.

A large number of calculations has been made for various bonds and groups by different authors, notably by Dadieu and Kohlrausch[3] and fair agreement with observations has been obtained. In the following table (Table V) are given different linkages with their characteristic oscillations, both calculated by the two formulæ and observed. The groups compared are C—H; C—C; C=C; $-\overset{H}{\underset{H}{C}}-$(transverse); H—CH=$CX_2$ and the structure

$$>C=\overset{|}{C}-C<_{|}$$

TABLE V.

Frequencies and Linkages.

No.	Type of Linkage	$\Delta\nu$ deduced from			$\Delta\nu$ observed		
		Binding Force	Thermal Dissociation	Group Effect	Isoprene	Dipentene	Ocimene
1	C—H (aliphatic)	2920	2988	..	2914 2981 3015	2685 2922 2971	2912 2983
2	C—H (aromatic)	3050	3118	..	..	..	..
3	$-\overset{H}{\underset{H}{C}}-$(transverse)	..	..	1200-1500	1382 1422	1207 1306 1375 1440	1235 1344 1376 1406 1440
4	H—CH=CX_2	..	..	3080	3092	..	3055
5	C—C (aliphatic)	890	900	..	899·8	879·2	885·4
6	C=C	1620	1635	..	1636	1610	1634
7	$>C=\overset{\|}{C}-C<_{\|}$	..	..	760 1070 1290	778 1066 1292	..	752 1069 1285

It is evident from the above table that the three compounds examined give the characteristic frequencies for C—H (aliphatic), C—C (aliphatic) and

[3] Kohlrausch, *Der Smekal-Raman Effect.*

C=C unmistakably in the correct regions and the transverse C—H oscillations have also come out in the three cases. The table further makes it evident that the shifts 3092 and 3055 observed in isoprene and ocimene which are too high for aliphatic C—H oscillations are really due to the presence in those compounds of the group $H \cdot CH : CX_2$. The group of frequencies 760, 1070 and 1290 characteristic of the structure $> C=C-C<$ comes out in the case of isoprene and ocimene but not in dipentene thus lending support to the chemical structure assigned to these compounds.

It is worthy of remark that in the case of ocimene there are two shifts in the C=C region, one having a value 1634 and the other 1666. There are in the ocimene molecule three double bonds of which two are conjugate as in isoprene while the third is simple. The conjugate double bonds give rise to the 1634 oscillation while the other one gives an exalted frequency probably due to the loading of the bond with the CH_3 and CH_2 radicles.[4] The intensity of the 1634 oscillation is nearly twice that of the 1666 oscillation thus lending further support to the consideration that the former is due to the two conjugated double bonds while the latter is due to the simple bond.

It is interesting to note that dipentene, a compound known to possess a cyclic structure does not give the characteristic frequencies given by benzene or toluene. Like cyclo-hexane, dipentene has nothing in common with benzene except that there are six carbon atoms joined up in a ring. It is also well known that the properties of dipentene well accord with those of aliphatic compounds. Quite probably the ring structure in dipentene unlike that in benzene is a puckered one similar to that in cyclo-hexane with the carbon atoms not all in one plane. The non-benzenoid character of the ring in dipentene is independently borne out also by X-ray diffraction results.[5]

(*b*) *Relation to Infra-Red Absorption.*

It is well known that the Raman spectrum gives only the fundamental oscillations of a molecule, the harmonics and the combinations occurring very rarely or never at all. Such being the case, it would be of interest to compare the Raman spectra with the infra-red absorption spectra.

Unfortunately infra-red absorption data are not available at all for isoprene and ocimene while for dipentene the results of Coblentz[6] on *d*-limonene have been taken as not far different. The chemical structure of dipentene

[4] Daure, *Introduction a l'etude de l'effect Raman*, p. 70.
[5] V. I. Vaidyanathan, *Indian Journal of Physics*, 1929, **3**, 387.
[6] Coblentz, *Investigations of Infra-red Spectra*, 1905, p. 92.

and limonene is identical and further Hantzsch[7] has observed that with increasing purity the absorption of dipentene comes to agree with that of limonene. Table VI contains the infra-red peaks converted into frequencies along with the Raman lines given by dipentene. Coblentz has investigated this compound up to 15μ and hence it is impossible to answer satisfactorily for all low frequencies, lower than about 750. The letters in brackets indicate the strength of the absorption maxima while the figures in brackets indicate the intensity of the Raman lines.

TABLE VI.

Raman Frequencies and Infra-Red Absorption Frequencies—Dipentene.

No.	Infra-red Absorption		Raman Frequency ν cm.$^{-1}$	No.	Infra-red Absorption		Raman Frequency ν cm.$^{-1}$
	μ	Frequency ν cm.$^{-1}$			μ	Frequency ν cm.$^{-1}$	
1	..	..	636 (0.5)	11	8·35	1198 (*w.*)	1207 (3)
2	..	..	674 (0.5)	12	7·6	1315 (*w.*)	1307 (2)
3	..	..	714 (0.5)	13	7·2	1389 (*m.*)	1375 (2)
4	12·7	787 (*s.*)	760 (3)	14	6·95	1438 (*w.*)	1440 (2)
5	..	..	818 (0.5)	15	6·2	1610 (*m.*)	1610 (6)
6	11·3	885 (*v.s.*)	879 (3)	16	6·05	1652 (*m.*)	1673 (1)
7	10·5	952 (*w.*)	..	17	5·2	1923 (*v.w.*)	..
8	9·7	1030 (*m.*)	1051 (0.5)	18	3·9	2563 (*w.*)	..
9	8·9	1123 (*m.*)	..	19	3·45	2898 (*s.*)	2869 (2) 2922 (2) 2972 (2)
10	8·7	1149 (*w.*)	..				

(Letters in the third and seventh columns signify the following :—*v.s.*, very strong; *s.*, strong; *m.*, medium; *w.*, weak; *v.w.*, very weak.)

It is well known that the symmetric oscillations involving no change in the electric moment of the molecule come out in great strength in Raman spectra while they are entirely absent in the infra-red absorption spectra, *e.g.*, 992 of benzene. It is also well known that certain frequencies occurring in the infra-red but not in scattering can be explained as combinations of some fundamentals.

[7] Hantzsch, *Ber. Deuts. Chem. Gess.*, 1912, **45** (1), 553.

Any oscillation of dipentene, a highly unsymmetrical molecule, will produce large changes in the electric moment of the molecule and as such we should expect that all the Raman frequencies will be fairly well represented in the infra-red absorption. The table shows good general agreement both in number and shifts.

The maximum 2563 in the infra-red has no analogue in the Raman spectrum. This can be interpreted as a combination of 879 and 1673 (=2552), two oscillations of the molecule, one of which is the C—C. The other neighbouring infra-red maximum at 1923 can also be interpreted as a combination of the C—C oscillation 879 with a minor oscillation 1051 making the combination tone equal to 1930. The absence in the Raman spectrum of the infra-red maxima at 1149 and 952 may be explained by the fact that they are quite weak in the absorption itself and might come out probably after very long exposure in scattering. It is rather difficult to understand why the infra-red frequency at 1123 which is of moderate intensity in absorption does not come out in the Raman spectrum, especially as no combinations with low frequencies usually occur. The Raman frequency 818 does not come out in the infra-red probably because it is a very weak oscillation even in scattering and perhaps a very careful investigation in this region of absorption might show a weak maximum. Evidently it cannot be a symmetric oscillation, being very weak in scattering itself.

The general agreement, however, is quite satisfactory.

The author wishes to record his grateful thanks to his professor, Sir C. V. Raman, Kt., F.R.S., N.L., for his kind guidance and interest in the course of the work and to Mr. S. Parthasarathy for very valuable help in the discussion.

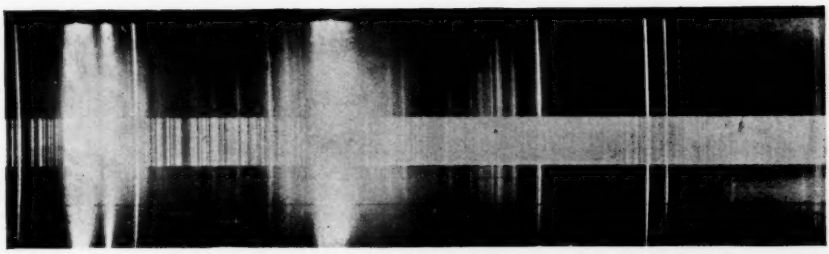


FIG. 1. Isoprene.

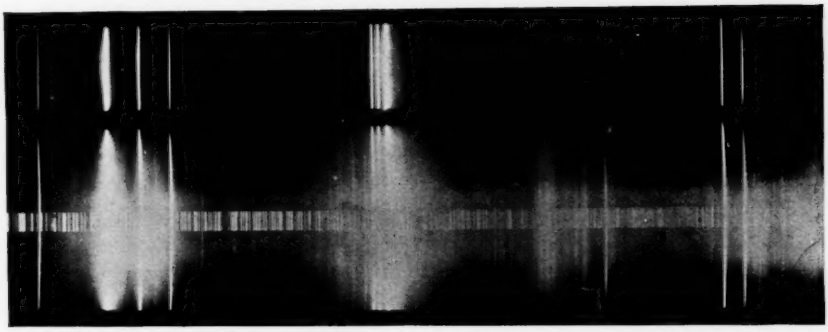


FIG. 2. Dipentene.

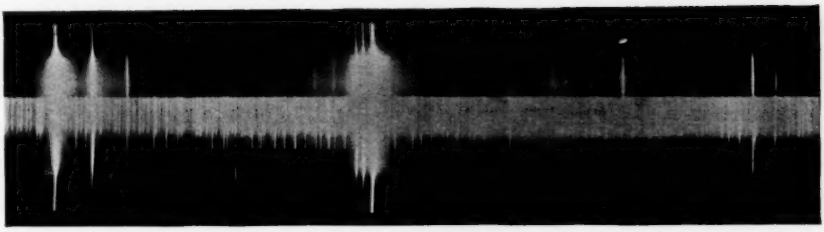


FIG. 3. Ocimene.

RAMAN SPECTRA.

ANALYSIS OF THE SPECTRUM OF TREBLY IONISED ZINC : Zn IV.

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Central College, University of Mysore, Bangalore.

Received June 20, 1935.
(Communicated by Prof. B. Venkatesachar, M.A., F.Inst.P.)

The spectrum of trebly ionised Zinc should be similar to that of trebly ionised Mercury and Cadmium. An analysis of the Hg IV spectrum was reported some time ago[1]; the present paper is concerned with an analysis of Zn IV. Cd IV has also been analysed and will be published shortly.

The wave-length data have been taken from R. O. Hutchinson.[2] These measurements are not accurate and the wave-lengths differ sometimes from those of Laporte and Lang[3] by more than 0·5 Å in the region common to the two. A similar error is even more serious in the case of Zn IV lines which are of shorter wave-length. Accordingly the common differences sometimes vary by as much as 40 cm.$^{-1}$ so that mere recurring differences are not to be relied on for purposes of classification. A consideration of the intensity and completeness of the multiplets is a surer indication of the correctness of the analysis. Another criterion is furnished by the question whether almost all the lines in the appropriate region are covered by the scheme. Thus the extreme ultraviolet spectra may be divided up into consecutive regions which belong almost exclusively to one stage in a series of successive stages of ionisation. A correct analysis embraces almost all the lines in one of these regions without leaving serious gaps. This is no doubt due to the fact that in any stage of ionisation only the low and middle levels are excited so that stray lines due to high levels not included in the classification and obtruding amongst the classified lines are quite rare. Though some apparently correct multiplets may be found by chance on account of the unreliability of the constant differences, all the important lines will not conform to the classification unless the intervals have been correctly chosen. Thus the region from λ 1768 to λ 1457 is almost wholly made up of Zn III lines and the correctness of the analysis is shown by the fact that the low and middle terms account for nearly all these lines. Similarly the spectrum of Hg IV was found to embrace nearly all the lines in the region λ 1658 to λ 1100 as combinations between low and

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[1] *Proc. Ind. Acad. Sci.*, 1934, **1**, 39.

[2] *Astrophys. Jour.*, 1923, **58**, 280.

[3] *Phys. Rev.*, 1927, **30**, 328.

TABLE I.

		d^8s				d^7s^2			
		$^4F_{9/2}$	$^4F_{7/2}$	$^4F_{5/2}$	$^4F_{3/2}$	$^4F_{9/2}$	$^4F_{7/2}$	$^4F_{5/2}$	$^4F_{3/2}$
d^8p	$^4F^\circ_{9/2}$	(4) 81719 *5938* (1) 75781 *3041* *3034*	..	..		(4) 79170 *5057* (1) 74113 *3053* *3065*	..	..	
	$^4F^\circ_{7/2}$	(1) 84760 *5945* (3) 78815 *3298* (0) 75517 *1817* *1835*	..			(1) 82223 *5045* (3) 77178 *1805*	?	..	
	$^4F^\circ_{5/2}$	..	(0) 80632 *3280* (3) 77352 *2725* (1) 74627 *1178* *1171*			..	(3) 78983 *2319* (1) 76664 *1032* (2) 75632 *1187* *1197*		
	$^4F^\circ_{3/2}$	..	..	(1) 78530 *2732* (2) 75798		..	..	(1) 77851 *1022* (1) 76829	
d^8p	$^4G^\circ_{11/2}$	(4) 79751 *3534*	..	..	..				
	$^4G^\circ_{9/2}$	(2) 83285 5933 (3) 77352* *4013* *4015*		..	..				
	$^4G^\circ_{7/2}$	(2) 87298 *5931* (3) 81367* *3291* (1) 78076 *3667* *3643*			..				
	$^4G^\circ_{5/2}$	..	(3) 85034 *3315* (4) 81719* *2736* (3) 78983*						
d^8p	$^4D^\circ_{7/2}$	(1) 82447 *5942* (2) 76505 *3299* (1) 73206 *3463* *3458*			..				
	$^4D^\circ_{5/2}$	..	(1) 79968 *3304* (1) 76664* *2754* (1) 73910 *1412* *1431*						
	$^4D^\circ_{3/2}$	..	..	(1) 78076* *2735* (0) 75341 *1323*					
	$^4D^\circ_{1/2}$	..	..	..	(1) 76664*				

* Blend.

middle terms. After a few trials an arrangement of multiplets was found in Zn IV which had this satisfactory property of including almost all the lines in the region from λ 1443 to λ 1030. The multiplets are given in Table I. Some combinations are represented by blends with others; this is due to insufficient resolution as can be easily seen by the fact that four pairs of close lines resolved by Laporte and Lang have been noted as single by Hutchinson. The terms deduced from these multiplets are given in Table II. By extend-

TABLE II. *Term Values in Zn IV.*

Configuration	Term	Value	Configuration	Term	Value
$3d^8 4s$	$^4F_{9/2}$	0	$3d^8 4p$	$^4G^\circ_{11/2}$	79751
	$^4F_{7/2}$	5938		$^4G^\circ_{9/2}$	83291
	$^4F_{5/2}$	9230		$^4G^\circ_{7/2}$	87299
	$^4F_{3/2}$	11962		$^4G^\circ_{5/2}$	90959
$3d^7 4s^2$	$^4F_{9/2}$	2539	$3d^8 4p$	$^4F^\circ_{9/2}$	81713
	$^4F_{7/2}$	7596		$^4F^\circ_{7/2}$	84757
	$^4F_{5/2}$	9915		$^4F^\circ_{5/2}$	86579
	$^4F_{3/2}$	10942		$^4F^\circ_{3/2}$	87759
$3d^8 4s$	$^2F_{7/2}$	11240	$3d^8 4p$	$^4D^\circ_{7/2}$	82443
	$^2F_{5/2}$	13840		$^4D^\circ_{5/2}$	85898
$3d^8 4s$	$^4P_{5/2}$	12550		$^4D^\circ_{3/2}$	87311
	$^4P_{3/2}$	16610		$^4D^\circ_{1/2}$	88603
	$^4P_{1/2}$	17630	$3d^8 4p$	$^2F^\circ_{7/2}$	94858
$3d^9$?	$^2D_{5/2}$?	−10512		$^2F^\circ_{5/2}$	99267

ing the classification to include the lines given by Bloch and Bloch[4] in the visible and near ultraviolet it is hoped shortly to improve the accuracy of these terms. Since no Rydberg sequences have been found and so no absolute term values are known, there is no point in drawing a $\sqrt{\frac{\nu}{R}}$ diagram. The course of the $d^8s\,^4F_{9/2} - d^8p\,^4F_{9/2}{}^\circ$ &c. lines and the various intervals in the iso-electronic-sequence Co I[5], Ni II[5], Cu III[6] and Zn IV are, however, given in Tables III and IV. Table V gives all the classified lines with their assignments.

[4] *Jour. de Physique*, 1934, **5**, 289.
[5] Goudsmit and Bacher, *Atomic Energy States*, McGraw Hill Co.
[6] B. V. Raghavendra Rao, *Zs. f. Phys.*, 1934, **88**, 135.

TABLE III.

Combination	Co I	Diff.	Ni II	Diff.	Cu III	Diff.	Zn IV
$d^8s\,^4F_{9/2}-d^8p\,^4F^\circ_{9/2}$ ..	29359	16804	46163	18384	64547	17166	81713
$d^8s\,^4F_{9/2}-d^8p\,^4G^\circ_{9/2}$ ..	28982	15989	44971	..	..	..	83291
$d^8s\,^4F_{7/2}-d^8p\,^4D^\circ_{7/2}$ ..	..	..	42228	..	..	..	76505

TABLE IV.

Term	Co I	$\Delta\nu$	Ni II	$\Delta\nu$	Cu III	$\Delta\nu$	Zn IV	$\Delta\nu$
$d^8s\ ^4F_{9/2}$	3482·76		8392·9		0		0	
		−659·85		−936·4		−1745		−5938
$^4F_{7/2}$	4142·61		9329·3		1745		5938	
		−547·49		−785·4		−1330		−3292
$^4F_{5/2}$	4690·10		10114·7		3075		9230	
		−385·65		−584·3		−855		−2732
$^4F_{3/2}$	5075·75		10663·0		3930		11962	
$d^8s\ ^2F_{7/2}$	7442·39		13549·1		7065		11240	
		−1018·38		−1445·3		−1745		−2600
$^2F_{5/2}$	8460·77		14994·4		8810		13840	
$d^8s\ ^4P_{5/2}$	13795·44		25034·6		..		12550	
		−240·76						−4060
$^4P_{3/2}$	14036·20		24786·9		..		16610	
		−362·95						−1020
$^4P_{1/2}$	14399·15		24834·7		..		17630	
$d^8p\ ^4G^\circ_{11/2}$	32430·56		53495·6		..		79751	
		−34·10						−3540
$^4G^\circ_{9/2}$	32464·66		53364·0		..		83291	
		−708·64						−4008
$^4G^\circ_{7/2}$	33173·30		54261·5		..		87299	
		−501·02						−3660
$^4G^\circ_{5/2}$	33674·32		55017·6		..		90959	
$d^8p\ ^4F^\circ_{9/2}$	32841·91		54556·1		64547		81713	
		−315·17		−860·6		−1480		−3044
$^4F^\circ_{7/2}$	33466·78		55416·7		66027		84757	
		−479·03		−657·3		−758		−1822
$^4F^\circ_{5/2}$	33945·81		56074·0		66785		86579	
		−250·30		−349·4		−462		−1180
$^4F^\circ_{3/2}$	34196·11		56423·4		67247		87759	
$d^8p\ ^4D^\circ_{7/2}$	..		51556·9		..		82443	
				−1180·5				−3455
$^4D^\circ_{5/2}$	..		52737·4		..		85898	
				−895·5				−1413
$^4D^\circ_{3/2}$	..		53633·9		..		87311	
				−541·0				−1292
$^4D^\circ_{1/2}$	..		54174·9		..		88603	
$d^8p\ ^2F^\circ_{7/2}$	35450·51		57079·1		66342		94858	
		−879·28		−1412·7		−2023		−4409
$^2F^\circ_{5/2}$	36329·79		58491·8		68365		99267	

TABLE V.

List of Classified Lines of Zn IV.

Int.	Wave-length	Wave-number	Classification
2	1443·0	69300	$d^8s\ {}^4P_{3/2}-d^8p\ {}^4D^\circ_{5/2}$
0	1434·8	69696	$d^8s\ {}^4P_{1/2}-d^8p\ {}^4D^\circ_{3/2}$
1	1430·7	69896	$d^8s\ {}^4P_{5/2}-d^8p\ {}^4D^\circ_{7/2}$
0	1414·4	70701	$d^8s\ {}^4P_{3/2}-d^8p\ {}^4D^\circ_{3/2}$
1	1409·1	70967	$d^8s\ {}^4P_{1/2}-d^8p\ {}^4D^\circ_{1/2}$
1	1388·8	72005	$d^8s\ {}^4P_{3/2}-d^8p\ {}^4D^\circ_{1/2}$
3	1387·8	72057	$d^8s\ {}^2F_{5/2}-d^8p\ {}^4D^\circ_{5/2}$ $d^8s\ {}^2F_{7/2}-d^8p\ {}^4G^\circ_{9/2}$
2	1374·8	72738	$d^8s\ {}^2F_{5/2}-d^8p\ {}^4F^\circ_{5/2}$
1	1366·0	73206	$d^8s\ {}^4F_{5/2}-d^8p\ {}^4D^\circ_{7/2}$
1	1362·9	73373	$d^8s\ {}^4P_{5/2}-d^8p\ {}^4D^\circ_{5/2}$
2	1360·2	73519	$d^8s\ {}^2F_{7/2}-d^8p\ {}^4F^\circ_{7/2}$
1	1353·0	73910	$d^8s\ {}^2F_{5/2}-d^8p\ {}^4F^\circ_{3/2}$
1	1349·3	74113	$d^7s^2\ {}^4F_{7/2}-d^8p\ {}^4F^\circ_{9/2}$
1	1340·0	74627	$d^8s\ {}^4F_{3/2}-d^8p\ {}^4F^\circ_{5/2}$
0	1327·3	75341	$d^8s\ {}^4F_{3/2}-d^8p\ {}^4D^\circ_{3/2}$
0	1324·2	75517	$d^8s\ {}^4F_{5/2}-d^8p\ {}^4F^\circ_{7/2}$
2	1322·2	75632	$d^7s^2\ {}^4F_{3/2}-d^8p\ {}^4F^\circ_{5/2}$
1	1319·6	75781	$d^8s\ {}^4F_{7/2}-d^8p\ {}^4F^\circ_{9/2}$
2	1319·3	75798	$d^8s\ {}^4F_{3/2}-d^8p\ {}^4F^\circ_{3/2}$
2	1307·1	76505	$d^8s\ {}^4F_{7/2}-d^8p\ {}^4D^\circ_{7/2}$
1	1304·4	76664	$d^8s\ {}^4F_{5/2}-d^8p\ {}^4D^\circ_{5/2}$ $d^7s^2\ {}^4F_{5/2}-d^8p\ {}^4F^\circ_{5/2}$
1	1301·6	76829	$d^7s^2\ {}^4F_{3/2}-d^8p\ {}^4F^\circ_{3/2}$
3	1295·7	77178	$d^7s^2\ {}^4F_{7/2}-d^8p\ {}^4F^\circ_{7/2}$
3	1292·8	77352	$d^8s\ {}^4F_{7/2}-d^8p\ {}^4G^\circ_{9/2}$ $d^8s\ {}^4F_{5/2}-d^8p\ {}^4F^\circ_{5/2}$
1	1284·5	77851	$d^7s^2\ {}^4F_{5/2}-d^8p\ {}^4F^\circ_{3/2}$
1	1280·8	78076	$d^8s\ {}^4F_{5/2}-d^8p\ {}^4G^\circ_{7/2}$ $d^8s\ {}^4F_{5/2}-d^8p\ {}^4D^\circ_{3/2}$

TABLE V (*contd.*)

Int.	Wave-length	Wave-number	Classification
1	1273·4	78530	$d^8s\ {}^4F_{5/2}—d^8p\ {}^4F^\circ_{3/2}$
3	1268·8	78815	$d^8s\ {}^4F_{7/2}—d^8p\ {}^4F^\circ_{7/2}$
3	1266·1	78983	$\left\{\begin{matrix} d^8s\ {}^4F_{3/2}—d^8p\ {}^4G^\circ_{5/2} \\ d^7s^2\ {}^4F_{7/2}—d^8p\ {}^4F^\circ_{5/2} \end{matrix}\right\}$
4	1263·1	79170	$d^7s^2\ {}^4F_{9/2}—d^8p\ {}^4F^\circ_{9/2}$
4	1253·9	79751	$d^8s\ {}^4F_{9/2}—d^8p\ {}^4G^\circ_{11/2}$
1	1250·5	79968	$d^8s\ {}^4F_{7/2}—d^8p\ {}^4D^\circ_{5/2}$
0	1240·2	80632	$d^8s\ {}^4F_{7/2}—d^8p\ {}^4F^\circ_{5/2}$
0	1234·4	81011	$d^8s\ {}^2F_{5/2}—d^8p\ {}^2F^\circ_{7/2}$
3	1229·0	81367	$d^8s\ {}^4F_{7/2}—d^8p\ {}^4G^\circ_{7/2}$
4	1223·7	81719	$\left\{\begin{matrix} d^8s\ {}^4F_{9/2}—d^8p\ {}^4F^\circ_{9/2} \\ d^8s\ {}^4F_{5/2}—d^8p\ {}^4G^\circ_{5/2} \end{matrix}\right\}$
1	1216·2	82223	$d^7s^2\ {}^4F_{9/2}—d^8p\ {}^4F^\circ_{7/2}$
1	1212·9	82447	$d^8s\ {}^4F_{9/2}—d^8p\ {}^4D^\circ_{7/2}$
2	1200·7	83285	$d^8s\ {}^4F_{9/2}—d^8p\ {}^4G^\circ_{9/2}$
2	1195·8	83626	$d^8s\ {}^2F_{7/2}—d^8p\ {}^2F^\circ_{7/2}$
1	1179·8	84760	$d^8s\ {}^4F_{9/2}—d^8p\ {}^4F^\circ_{7/2}$
3	1176·0	85034	$d^8s\ {}^4F_{7/2}—d^8p\ {}^4G^\circ_{5/2}$
1	1170·6	85426	$d^8s\ {}^2F_{5/2}—d^8p\ {}^2F^\circ_{5/2}$
2	1145·5	87298	$d^8s\ {}^4F_{9/2}—d^8p\ {}^4G^\circ_{7/2}$
1	1136·0	88028	$d^8s\ {}^2F_{7/2}—d^8p\ {}^2F^\circ_{5/2}$
3	1049·8	95256	$d^9\ {}^2D_{5/2}—d^8p\ {}^4F^\circ_{7/2}$
2	1037·4	96395	$d^9\ {}^2D_{5/2}—d^8p\ {}^4D^\circ_{5/2}$
2	1029·9	97097	$d^9\ {}^2D_{5/2}—d^8p\ {}^4F^\circ_{5/2}$

THE RAMAN SPECTRA OF IODIC ACID AND THE ALKALINE IODATES AS SOLIDS AND SOLUTIONS.

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1. Introduction.

The study of progressive dissociation of electrolytes in solution by the method of light-scattering was for the first time made use of by I. R. Rao[1] in his investigations on Raman spectra in different concentrations of nitric acid. He has shown that the lines arising from the nitrate ion in solution, first increase in intensity as the concentration is decreased up to a certain point and then become less intense and weak for greater dilutions. In higher concentrations of the acid there are other lines present (some of them fairly strong), which become weaker and weaker and finally disappear as the dilution is gradually increased. It has been pointed out that these lines are to be attributed to the undissociated molecule and that as the dissociation progresses their intensity diminishes while the nitrate lines gain in intensity in a proportionate manner. Thus a comparative study of the Raman effect in different concentrations of an acid provides a beautiful picture of the progress of electrolytic dissociation of its molecules in solution. The method is particularly suitable for concentrated solutions of strong electrolytes for which no other reliable method is available.

Of the systems hitherto studied by this method, nitric acid and sulphuric acid have received the greatest attention, because of their striking and fruitful results. Iodic acid is known to be a strong acid like nitric acid and to contain undissociated molecules even in dilute solutions.[2, 3] Its Raman spectrum has been studied, but not in sufficient detail, and the results obtained by the previous investigators[4, 5, 6, 7, 8] are found to be discordant

1 Ramakrishna Rao, I., *Proc. Roy. Soc.*, (A), 1930, **127**, 279.
2 Kraus and Parker, *Jour. Amer. Soc.*, 1922, **44**, 2429.
3 Murray and Hartley, *Proc. Roy. Soc.*, (A), 1929, **126**, 84.
4 Krishnamurti, P., *Ind. Jour. Phys.*, 1930, **5**, 633.
5 Raman Nayar, M., and Premanath Sharma, *Zeit. f. anorg. u. allg. Chem.*, 1934, **220**, 169.
6 Nisi, *Jap. Jour. Phys.*, 1929, **5**, 119.
7 Dickinson and Dillon, *Proc. Nat. Acad. Sci.*, 1929, **50**, 334.
8 Woodward, L. A., *Phys. Zeits.*, 1931, **32**, 690.

and their conclusions appear to be based upon incomplete data. Comparatively little attention has also been paid in the past to the study of the Raman effect in iodates. The present investigation was undertaken with a view to clarify the position and obtain a complete Raman spectrum of the acid and its salts which would throw some light on their structure and chemical constitution.

2. *Experimental Details.*

The experimental arrangement that was made use of in the following investigation was the same as that described by the author in a previous communication.[9] In order to keep the alignment of the tube and the spectrograph undisturbed, the apparatus was so designed that the solution could be changed without altering the position of the tube. The Fuess glass spectrograph used in the investigation had a dispersion of about 20 A.U. per millimetre in the 4358 A.U. region and gave satisfactory spectra.

The substances used were supplied by Kahlbaum and marked "analytical". They were further purified by two or three crystallisations. Lithium iodate was prepared by the neutralisation of lithium hydroxide by iodic acid and crystallised out of the solution. Potassium bi-iodate was available only in the state of fine powder and it was used as such without further purification. In spite of the fact that the sodium and lithium iodates as well as the potassium bi-iodate were in a state of fine powder, reasonably good pictures were obtained. The best spectrum, however, was obtained with crystals of less than two millimetres each way in size. Larger crystals were not suitable for the reason that the reflection from the surfaces became greater and increased the intensity of the exciting line, thus rendering the spectrum over-exposed. The spectrograms were taken on Ilford Hypersensitive Panchromatic plate H and D 2500 and measured by means of a Hilger wavelength micrometer. The wavelengths of the modified lines were calculated by linear interpolation from the nearest known lines in the iron arc comparison spectrum.

3. *Results.*

Typical photographs of the spectra obtained are reproduced in the accompanying Plates. The scattered spectra of iodic acid and of the iodates were fairly intense. The acid was examined both in the state of small crystals and in solutions of a wide range of concentrations varying from 18 N to 0·15 N. The best solid picture was obtained at an exposure of about two hours; but plates were also taken at exposures of six and twelve hours in order to bring out some of the fainter lines more prominently. Several

[9] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, (A), 1935, **1**, 850.

exposures were made with the solid at different stages of crystallisation in order to make sure that the lines obtained were genuine. The exposure time for the most concentrated solution was two hours and the exposures for the other concentrations were increased in proportion to the dilution. The results obtained for the crystalline solid along with the visual estimates of intensity are given in Table I and those for the solutions are given in

TABLE I.

Iodic acid crystal.

Exciting line	Raman lines		Intensity	Others	
	ν	$\Delta\nu$ in cm.$^{-1}$		Krishnamurti[4]	Nayar and Sharma[5]
4358·3 A.U.	21541	1397	0		
$\nu = 22938$	21689	1249	0		
	22096	842	2		
	22115	823	0		
	22137	801	0		
	22156	$\overline{782}$	10	780.7 st.	799.15 m.
	22200	739	1		
	22226	$\overline{713}$	8	712.6 v. st.	757.8 st.
	22268	670	0		
	22286	652	0		
	22306	$\overline{633}$	6	633 st.	640.6 w.
	22525	413	1		
	22561	377	3		
	22610	328	6	327 m.	473.75 w.
	22624	314	0		
	22643	295	1		
	22718	220	1		262.78 v. w.
	22740	198	0		
	22775	163	0		
	22810	128	1		
	22823	115	0		
	22842	97	0		
	22858	80	1		
	22875	64	1		

A dash above some of the frequency numbers indicates that the anti-stokes of those lines were also present. The letters included within the brackets against some of the numbers in this table as well as in the subsequent ones indicate the strength of the line, *viz.*, *st.* = strong, *v. st.*=very strong; *m.*=medium strong; *w.*=weak; *v. w.*=very weak; *br.*=broad; *v. br.*= very broad; *d.*=diffuse; and *sh.*=sharp.

Table II. The frequency shifts for the iodates of lithium, sodium and potassium are given in Table IV and those for the bi-iodate of potassium in Table V. The Raman lines are in general obtained by 4046, 4358, and

TABLE II.

Iodic acid solutions (aqueous).

Exciting line 4358·3 A.U. Raman frequencies in cm.$^{-1}$

18 N	12 N	6 N	4·5 N	3 N	1·5 N	0·5 N	0·15 N
1392 w.	1392 v. w.	..	..	..	..	..	..
1238 w.	1238 v. w.	..	..	..	..	..	..
823 st.	823 st.	823 m.	823 m.	823 m.	819 w.	819 v. w.	..
779 v. st.; v. br.	783 v. st.; v. br.	789 v.st.;br.	789 st. br.	796 st.	796 m.	800 v. w.	..
..	..	796 st.	796 st. sh.	798 st. sh.	799 st. sh.	802 m.sh.	802 w. sh.
644 m.br.	644 st. br.	644 m. br.	644 m. br.	644 m.	644 w.	644 v. w.	..
463 m.	463 w.	463 v. w.	..	..	..	..	..
334 st. ; v. br.	334 v. st.; v. br.	330 st. br.	330 m. br.	328 w.	328 v. w.	328 v. w.	..

TABLE III.

Comparison table. Raman frequencies in cm.$^{-1}$

Author 18 N	Nisi[6] 0.6 N	Dickinson and Dillon[7] 2.7 N	Woodward[8] 10 N—0.8 N	Nayar and Sharma[5] 5 N
1392 w.				
1238 w.				
823 st.				
779 v. st.; v.br.	805 st. 799 m.	800 st.	796 v. st.	821.68 v. st.
644 m.br.	..	..	649 st.	659.01 w.
463 m.	393 w.	..	..	..
334 st.; v. br.	317 w.	329 m.	335 m.	358.05 w.

5461 radiations of the mercury arc ; but only the values obtained for the 4358 A.U. as exciting line, have been given in the tables. The shifts obtained with the other two lines are used as check on the values given.

The crystalline acid has yielded a number of lines many of which have not been reported previously. The frequency shifts obtained for the strong lines in the solid are in good agreement with those given by Krishnamurti.[4]

TABLE IV. *Alkali Iodates.*

Substance	Exciting line	Raman lines		Intensity	Others	
		ν	$\Delta\nu$ in cm.$^{-1}$		Krishnamurti, $\Delta\nu$ in cm.$^{-1}$	Nayar & Sharma $\Delta\nu$ in cm.$^{-1}$
KIO_3 (crystal)	4358·3 ν=22938	22130	808	medium	808 m.	807.5 m.
		22149	789	medium	784 m.	..
		22185	753	very strong	751.4 v.st	
		22201	737	very strong	733 st.	759 st.
		22598	341	weak		
		22603	335	weak		
		22630	308	weak		
		22806	132	very weak & broad		
		23677	739	weak		
		23691	753	weak		
		23726	788	very weak		
		23745	807	very weak		
KIO_3 (soln.) (0·25 N at 30°C.)	4358·3 ν=22938	22143	795	strong		
		22616	322	very weak		
KIO_3 (soln.) (1.0 N at 90°C.)	,,	22135	803	strong		
		22605	333	weak		
		23740	802	very weak		
$NaIO_3$ (solid)	4358·3 ν=22938	22129	809	medium		
		22151	787	weak		
		22200	738	strong		
		22218	720	very weak		
$NaIO_3$ (soln.) (0.25 N at 30°C.)	,,	22142	796	strong		796 st.[7]
		22614	324	very weak		

Substance	Exciting line	Raman lines		Intensity
		ν	$\Delta\nu$ in cm.$^{-1}$	
$LiIO_3$ (solid)	4358·3 ν=22938	22125	813	weak
		22139	799	strong
		22157	781	medium
		22173	765	very strong
		22330	608	very weak and broad
		22479	459	weak and broad
		22606	332	weak
		22629	309	strong
		22695	243	medium
		22769	169	weak
$LiIO_3$ (soln.) 3.4 N at 30°C.	,, ,,	22144	794	very strong
		22335	603	very weak and broad
		22515	423	very weak and broad
		22618	320	strong
$LiIO_3$ (soln.) 0.25 N at 30°C.	,, ,,	22141	797	strong
		22618	320	very weak

The plate shows the remarkable change that takes place in the spectrum as soon as it is dissolved in water. The sharp lines in the crystal are replaced in the solution by very broad bands which tend, however, to sharpen again as the concentration is decreased.

Table III gives a comparison of the results obtained by the author with those given by the previous investigators. It can be seen that some of the lines in the highest concentrations as well as certain anomalies in intensity and position of the lines observed by the author have not been obtained by the earlier experimenters. This is obviously due to the fact that they have

TABLE V.

Substance	Exciting line	Raman lines		Intensity
		ν	$\Delta\nu$ in cm.$^{-1}$	
Pot. bi-iodate	4358·3 ν=22938	21546	1392	very weak
		21695	1243	very weak
		22120	818	medium, sharp
		22165	773	strong, sharp
		22199	739*	weak, broad
		22305	633	weak
		22621	317	weak
Pot. bi-iodate (solution)	,, ,,	22141	797	strong

worked only with concentrations less than that at which these lines appear. Woodward[8] alone has worked with a 10 N solution in which 463 should have appeared very faintly. The single broad band at about 800 has been identified for the first time as a close doublet consisting of a broad band with the centre at 779 and a comparatively narrow one at 823. The author also has been unable to confirm the line 393 reported by Nisi[6] in his 10% solution. The results given by Nayar and Sharma,[5] both for the crystal and for solution, show large differences from those obtained by the author as well as by others and are evidently due to considerable errors in their measurements.

4. Evidence for Electrolytic Dissociation in Iodic Acid.

Figure 1 gives a schematic representation of the transition that takes place in the spectra of iodic acid when it goes from the state of solid to that of solutions of varying concentrations. The intensity of the Raman lines is represented approximately by the height of the dark lines. It can be seen from the figure that a direct correlation exists between the spectra of the solid and solutions. The whole series of spectra can be explained on the

* This is the frequency shift of the centre of the band which has a width of about 60 wave numbers.

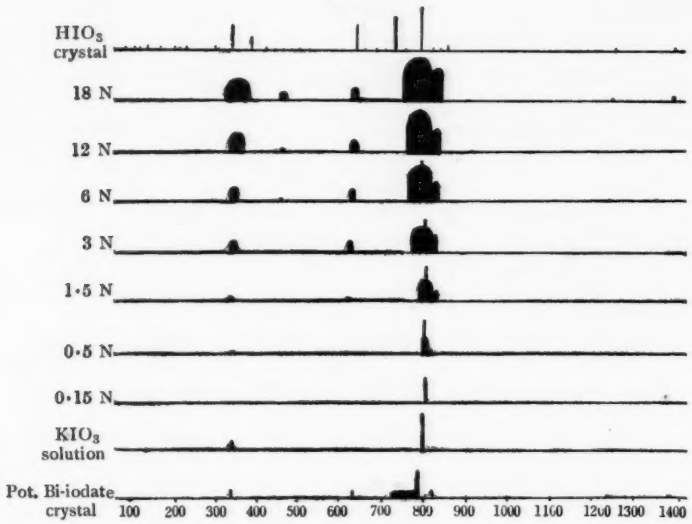

FIG. 1.

assumption that the crystalline acid consists of undissociated HIO_3 molecules and that the dissociation which is very small in concentrated solutions goes on gradually increasing as the concentration diminishes. Thus the sharp and intense lines of the acid at 782, 713, 633, 377 and 328 are due to the vibrations of the HIO_3 molecule. The two lines at 782 and 713 shift slightly to a higher frequency and broaden out, the two broad lines together thus appearing as a single broad band with the maximum at 779 and extending from about 730 to 815. In a similar way the lines at 377 and 328 give rise to the band at 334 covering both the lines. The band at 644 arises from the single line at 633 and is narrower than the other two as can be expected. As the concentration falls off, the number of undissociated molecules decreases and these bands gradually lose both in intensity and in breadth (Fig. 2). The band at 779 appears also to shift in position. The two lines at 1397 and 1249 which are present in the solid and in the 18 N solution do not appear in any other concentrations. There is also a band at 463 in the 18 N solution which diminishes in intensity very rapidly and is practically non-existent at about 4·5 N. These three lines are also to be attributed to the HIO_3 molecule.

At about a concentration of 6 N a fairly sharp line at 796 appears superposed on the band in that region and this goes on increasing in intensity relative to that of the band as the dilution increases. At about 0·5 N this is the strongest line in the spectrum as can be seen from Fig. 4 and the superposed

band is very weak. This line appears also very prominently in the solutions of alkali iodates and is evidently to be attributed to the IO_3 radical. The relative increase in the intensity of this line in the more dilute solutions indicates the progress of dissociation of the acid itself. The other line at 320 observed in the iodate solution is presumably superposed on the HIO_3 band at 334 ; but its effect on the band is too feeble to be observed. The fact that the band at about 800 persists even in solutions of about 0·5 N shows that the dissociation is incomplete even at such high dilutions.

5. Evidence for the Polymerisation of the Acid.

A large mass of chemical evidence[10,11] goes to show that iodic acid is polymerised to an appreciable extent in aqueous solutions ; but the existence of a few contradictory chemical facts keeps it still an open question. In their investigations on the Raman effect, Nayar and Sharma[5] have failed to elicit the band at 634 and 334 in very dilute solutions (0·2 N) and they, therefore, have pointed out that these two lines are due to the polymers of the acid. But in the investigations of the author these lines appear, though only feebly, in all dilutions and hence the conclusions of the above authors based upon this fact are not justified. There is, however, other evidence to show that I_2O_6'' ions exist in aqueous solutions. As can be seen from Fig. 1, the line at 823 which appears very prominently as a component to the strong band at 779, does not exist either in the solid iodic acid or in the spectrum of the iodates, but is present as a line of medium intensity in the bi-iodate of potassium. This line is, therefore, a positive proof for the existence of I_2O_6'' ions in iodic acid solutions. The intensity of this line goes on diminishing as the dilution increases, which shows that the polymerisation becomes gradually less. The faint appearance of this line even at a concentration of 0·5 N indicates that I_2O_6'' ions are present even in dilute solutions.

Though, generally, the Raman lines in the solutions of electrolytes are broader than in the solid which is attributed to the increased freedom of rotation of the ions in the solutions, the extraordinary breadth of these lines in the iodic acid solutions is unaccountable unless it is also attributed to the influence of the polymerised molecules themselves. This suggestion is justified by the fact that in the similar case of water, the Raman line corresponding to the fundamental oscillation of the molecule appears as a broad band consisting of three components, which has been shown by elaborate analysis[12] to be due to the highly polymerised state of the water molecule.

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[10] Gmelin's *Handbuch der Anorganische Chemie*, 1933, **8**, 419 J.

[11] Raman Nayar, M., and Gairola, T. R., *Zeit. f. anorg. u. allg. Chem.*, 1934, **220**, 163.

[12] Ramakrishna Rao, I., *Proc. Roy. Soc.*, (A), 1934, **145**, 489.

In order to examine whether the spectrum of the salt of the dibasic iodic acid shows any similarity to that of the solid or of the concentrated solution, the Raman spectrum of potassium bi-iodate has been investigated both as solid and solutions and the results are given in Table V. The spectrum of the solid resembles, in a general way, that of the iodic acid crystal. But there is the appearance of a line of medium intensity at 818 which is to be attributed to the I_2O_6 radical. The strong line at 713 in iodic acid has spread out into a band with its centre at 739 in the bi-iodate. This fact is very significant for two reasons. Firstly, it shows the effect of polymerisation on the line belonging to the HIO_3 molecule and substantiates our assumption regarding the finite width of bands in the acid solutions. Secondly, it is interesting because, usually crystals give only sharp lines and the appearance of this band in the solid is surprising. The solution of this salt (less than 0·1 N) has given only one line at 797 corresponding to the intense line of the IO_3 radical. From these we are led to conclude that while in the solid the acid salts of the iodic acid are complex compounds in which I_2O_6'' ions exist, in the aqueous solutions, the bi-iodates behave in the Raman effect, as if they are only mixtures of the acid and the alkali iodate.[13]

6. Structure of Iodates.

The fundamental vibrations of the molecules of the AX_3 type have been treated by Dennison[14], assuming a symmetrical pyramidal model. For this type, it has been shown that there are four normal modes of vibration, two of the normal vibrations with frequencies ν_1 and ν_2 being parallel to the axis of symmetry and the other two normal vibrations with frequencies ν_3 and ν_4 being perpendicular to the axis of symmetry (which are doubly degenerate). In the Raman effect ν_1 and ν_2 would appear stronger than ν_3 and ν_4 because the former are optically less active than the latter and ν_1 in which the X atoms execute symmetrical expansions and contractions in their plane while the A atom keeps vibrating along the symmetry axis, would come out as the most intense line. Following the ideas of Hund[15] it was later on shown by Dennison and Hardy[16] that in the case of the pyramidal molecule of the AX_3 type like NH_3,in which the A atom lies close to the plane of the X atoms the parallel vibrations ν_1 and ν_2 become double, the magnitude of the doublet separation depending generally on the height of the pyramid and on the frequency. If the A atom lies in the plane of the X atoms, that is, if the model is coplanar as in the case of the CO_3 or NO_3 radical, the splitting of the

[13] Walden, P., *Zeit. Phys. Chem.*, 1888, **2**, 64.
[14] Dennison, *Phil. Mag.*, 1926, **1**, 195.
[15] Hund, F., *Zeit. f. Phys.*, 1927, **43**, 805.
[16] Dennison and Hardy, *Phys. Rev.*, 1932, **39**, 938.

symmetrical oscillations do not take place and the totally symmetrical oscillation which does not involve any change in the electric moment, is optically inactive and appears very strongly in the Raman effect, while the other symmetrical oscillation perpendicular to the plane does not appear at all in the Raman effect. The splitting of the vibrational levels can also occur if there are accidental degeneracies among the frequencies as in the case of CCl_4, CS_2, CO_2, etc.

In the Raman spectra of the iodates we have found that one of the parallel vibrations splits up into a quadruplet and the other into a doublet or triplet and their probable significance will be discussed here.

Table IV gives the Raman frequencies observed for the iodates of lithium, sodium and potassium both in the state of crystals and solutions. A concentrated solution (3·4 N) of lithium iodate has yielded a very strong line at 794 and a fairly strong line at 320 and two weak lines at 423 and 603. In the crystals, all the three iodates give a strong group of four lines in the neighbourhood of 800 and another less prominent group at about 320. Lithium iodate shows also two broad bands at 459 and 608, which probably consist of unresolved components. Besides in the crystals of lithium iodate and potassium iodate as well as in the crystals of iodic acid, there exist a number of lines of lower frequency and these will be treated separately in the succeeding section. These four lines which occur in the iodates as also in the iodic acid evidently belong to the fundamental vibrations of the IO_3 group. Since all the four frequencies appear and both the parallel vibrations exhibit splitting, we are led to conclude that the IO_3 radical is pyramidal in structure with the I atom close to the plane of the O atoms. In such a case the two groups of lines at about 800 and 320 correspond to ν_1 and ν_2 respectively and the two faint lines at 608 and 459 correspond to ν_3 and ν_4 respectively. The infra-red data for potassium iodate gives the absorption frequencies at 781, 748 and 371.[17,18]

Though the relative shifts and intensities of the components differ widely from one component to another, the differences between the first two lower shifts and the last two higher shifts are almost equal and are of the same magnitude from compound to compound. These four components can be represented by the relation $\nu_1' = \nu_1 \pm \alpha \pm \beta$, where ν_1 is the average of all components, β is half the difference between one and two or three and four and α is half the difference between one and three or two and four. Table VI gives

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[17] Schaefer and Schubert, *Ann. der Phys.*, 1921, **7**, 309.

[18] Laski, *Zeits. f. Krist.*, 1927, **65**, 607.

the values of ν_1, a and β and the calculated values of frequencies together with the observed shifts of the components.

TABLE VI.

Substance	ν_1	a	β	Calculated				Observed			
				$\nu_1+a+\beta$	$\nu_1+a-\beta$	$\nu_1-a+\beta$	$\nu_1-a-\beta$	1	2	3	4
HIO_3	812	8·5	20·5	841	800	824	783	842 w.	801 v.w.	823 v.w.	782 st.
$LiIO_3$	789	7	16	812	780	798	766	813 w.	781 m.	799 st.	765 v.st.
$NaIO_3$	764	10	35	809	739	789	719	809 m.	739 st.	787 w.	720 w.
KIO_3	770	10	26	806	754	786	734	808 m.	753 v.st.	789 m.	737 st.

A tentative explanation for this interesting fact is given as follows. The vibrational energy levels with frequency ν_1 is split up in the first instance, to a doublet in accordance with the Hund-Dennison theory and is further split up, to form a quadruplet due to an accidental degeneracy $\nu_1=\nu_2+\nu_4$. In the case of lithium iodate where four frequencies are observed, this condition has been satisfied. That the parallel vibration with frequency ν_2 also shows splitting in all cases lends support to our postulate regarding the first split of ν_1. If the above explanation is valid, the height of the pyramid should be small enough to cause the splitting and the X-ray evidence[19, 20] seems to support it.

It should be remarked that the relative shifts and intensities of the components differ from compound to compound as illustrated in Fig. 5 and this is to be explained as due to the influence of the cation on the vibrations of the radical. That the cation in the solid aggregate has a great influence on the vibrations of this radical, is also demonstrated by the fact that in the solutions of all the iodates where the influence of the metal ion is considerably less, the components vanish giving place to strong lines of finite breadth. The vibration frequencies of lithium, sodium and potassium show also a small increase according to the increasing atomic weight. The strong line of lithium iodate likewise, appears to shift towards lower frequencies as the concentration increases. The effect of temperature on the main vibration frequency appears to be opposite to that of concentration as can be seen from the values given in Table IV, for potassium iodate solution at 30°C.

[19] Zachariasen, *Z. Krist.*, 1929, **71**, 501 and 517.
[20] Zachariasen and Barta, *Phys. Rev.*, 1931, **37**, 1626.

and 90°C. A detailed theoretical analysis of the spectra of the iodates is deferred to a later publication.

7. *Low Frequency Oscillations.*

A clear spectrum of the crystals of iodic acid shows besides the lines corresponding to the molecular structure described above, a number of lines with a maximum shift of about 220 (Fig. 6) in the neighbourhood of the exciting line, namely, 220, 198, 163, 128, 115, 197, 80 and 64. The antistokes of some of these lines are also faintly visible, but could not be measured because of the presence of the companions for the exciting line. Two similar low frequency shifts at 243 and 169 are also obtained for solid lithium iodate (Fig. 7) and only one at 132 for the potassium iodate crystals. These lines are completely washed out in solutions and there is an appearance of faint wings on either side of the exciting line. Similar low frequency oscillations have been observed previously by the earlier investigators in some crystals of carbonates,[21] and nitrates[22] and quite recently by Gross and Vuks[23] in the crystals of diphenyl, benzene and naphthalene and are explained as belonging to the lattice vibrations in the crystal. Thus, one possible explanation for these observed low frequency oscillations in the iodates is that they are connected with the vibrations of the layers of the atoms in the crystal lattice against each other. But it is hard to believe that the lattice is capable of oscillations giving rise to such a large number of lines as is the case with iodic acid. Another alternative explanation that may be put forward is on the lines suggested by Bhagavantam,[24] namely, that these low frequency oscillations are due to the oscillational motions or restricted rotations of the molecules in the solid state. The molecules possess greater freedom for rotation in solution and exhibit the phenomenon of wings. The whole theory of the so-called lattice vibrations is, however, in its infancy and no more can be said about them until a clearer picture of it is forthcoming.

In conclusion, the author wishes to express his grateful thanks to Prof. Sir C. V. Raman, F.R.S., N.L., for his helpful interest in the work. The author's thanks are also due to Dr. P. Krishnamurti for his keen interest in the work.

Summary.

The Raman spectrum of the iodic acid as a function of concentration and of the iodates of lithium, sodium and potassium in the state of the solid and solutions have been investigated. The crystals of iodic acid yield five

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[21] Bhagavantam, S., *Zeits. fur Kryst.*, 1931, **77**, 43.

[22] Cabannes and Canals, *Compt. Rend.*, 1931, **193**, 289.

[23] Gross and Vuks, *Nature*, 1935, **135**, 100; *Nature*, 1935, **135**, 431.

[24] Bhagavantam, S., *Ind. Jour. Phys.*, 1933, **8**, 197; see also Pauling, L., *Phys. Rev.*, 1930, **36**, 430.

intense lines and a number of weak and sharp lines, which are replaced by intense and broad bands in solution. The spectrum of the solutions for a very wide range of concentrations varying from 18 N to 0·15 N show an anomalous behaviour regarding intensity and frequency shifts. This fact has not been observed previously because the earlier authors had not worked with such high concentrations. From a qualitative study of the solid and solutions, evidence has been obtained for the progressive dissociation of the acid. The results show that the dissociation is incomplete even at concentrations of 0·5 N. Suggestions have also been put forward that the acid is polymerised in the solutions to an appreciable extent, the polymerisation decreasing with dilution.

The spectra of the iodates give in general two lines which are identified with the two possible parallel oscillations of the pyramidal form of the molecules of the AX_3 type and in the case of lithium iodate and iodic acid two more lines are obtained corresponding to the two perpendicular oscillations. The main parallel vibrations of the radical are split up into components in all the iodates including iodic acid, the relative shifts and intensities being different from compound to compound, the number of components being four in the case of ν_1 and two or three in the case of ν_2. The splitting of the vibration with the frequency ν_1 has been explained as partly due to the positional degeneracy pointed out by Hund and Dennison and as partly due to the accidental degeneracy, $\nu_1 = \nu_2 + \nu_4$. The shift and the relative intensities of these components are also shown to be influenced by the metal ion. The shift of the intense line in the solution depends to some extent on the cation, on concentration and on temperature.

A large number of low frequency oscillations has also been obtained in the crystals of iodic acid. Two such oscillations occur in the lithium iodate and only one in potassium iodate crystals. An explanation of these lines is briefly suggested.

Potassium bi-iodate crystal has given a spectrum somewhat similar to that of iodic acid. The presence of a new line in its spectrum indicates the existence of I_2O_5'' ions. The existence of a band in the spectrum of the solid is very significant. The solution of this salt behaves as if it were only a mixture of HIO_3 and KIO_3.

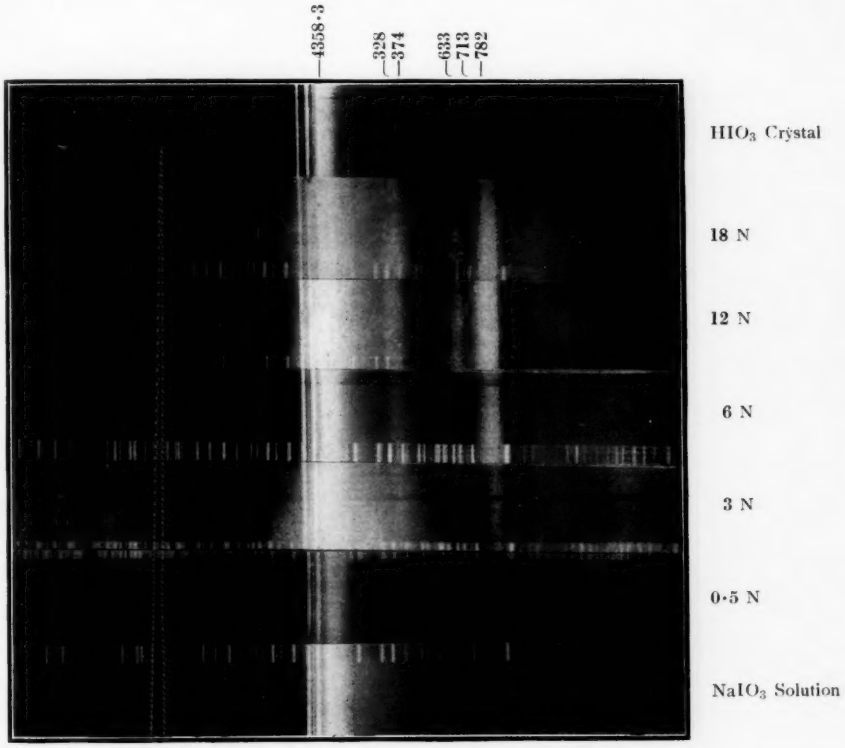

4358·3
328
374
633
713
782
HIO_3 Crystal
18 N
12 N
6 N
3 N
0·5 N
$NaIO_3$ Solution

FIG. 2.

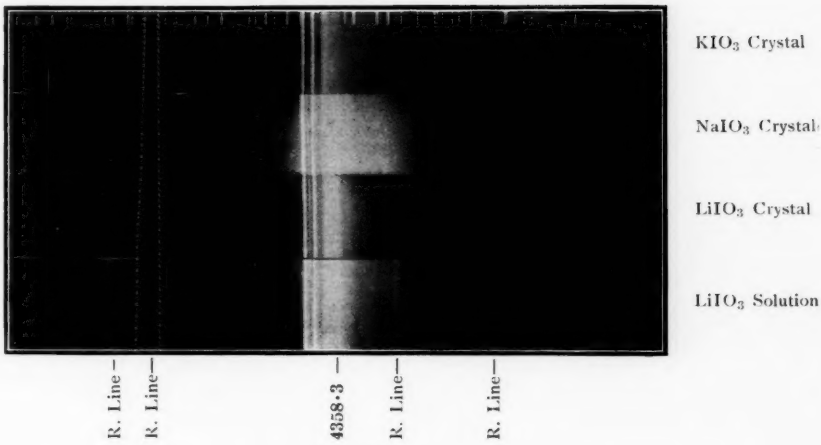

KIO_3 Crystal
$NaIO_3$ Crystal
$LiIO_3$ Crystal
$LiIO_3$ Solution
R. Line
R. Line
4358·3
R. Line
R. Line

FIG. 3.

FIG. 4. HIO_3 Solutions.

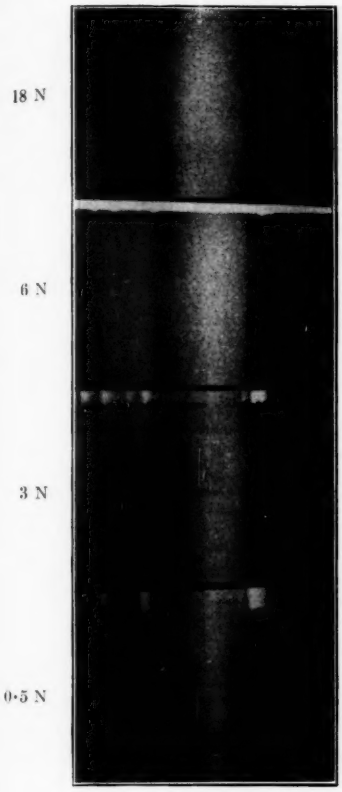
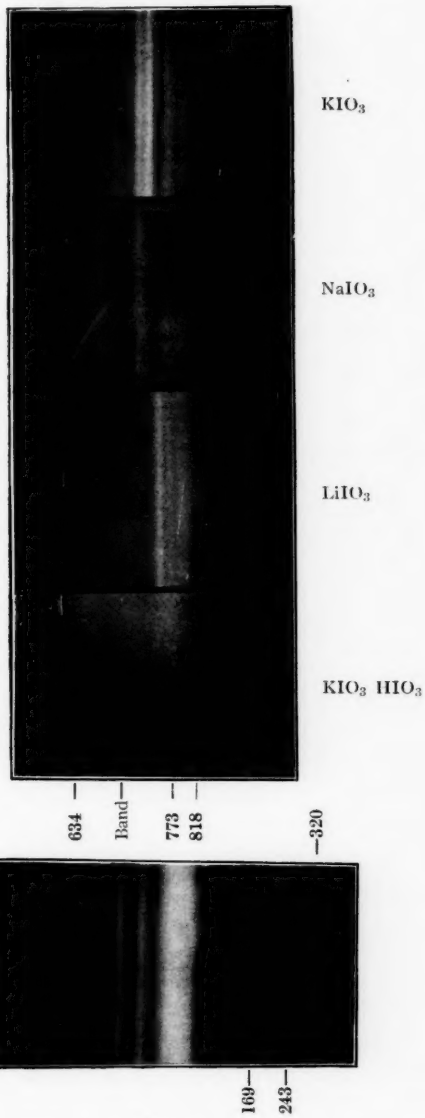


FIG. 5. Iodate Crystals.



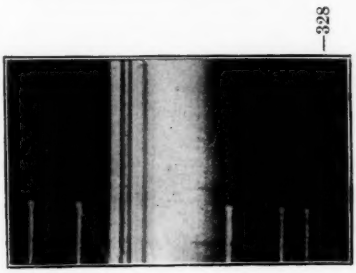


FIG. 6.
HIO_3 Solid showing low frequency oscillations.

FIG. 7.
$LiIO_3$ Solid showing low frequency oscillations.

ON THE CONVERGENCE ERROR IN DEPOLARISATION MEASUREMENTS.

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1. *Introduction.*

So much importance attaches to the precise measurement and interpretation of the degree of depolarisation of scattered light—be it in Tyndall, Rayleigh or Raman scattering—that no apology is needed for a paper dealing with a somewhat difficult point arising in the technique of such measurements, namely, the errors due to the lack of parallelism in the rays of light entering the medium and scattered by it. In practice it is not possible to realise the theoretical ideal of the illumination of the medium by a beam of parallel rays, and the examination of the scattered light in a direction strictly transverse to the latter. The comparatively feeble intensity of the scattered light usually entails the use of a source of finite dimensions and of a lens to concentrate the beam of light during its passage through the medium. In consequence the rays of light are neither parallel among themselves, nor strictly perpendicular to the direction of observation, and errors arise which may assume great importance when considering relatively small depolarisations.

There has been considerable divergence of opinion regarding the magnitude of the errors arising in the manner referred to above, and particularly in the case when an illuminating lens of large aperture is used to focus an image of the source of light within the medium at the point of observation. It is obvious that the rays starting from a given point on the source and reaching the conjugate point in the focal plane are optically coherent with each other. Dr. I. Ramakrishna Rao[1] took this coherence into account and claimed that no correction is necessary to the observed value of the depolarisation on account of the finite aperture of the lens provided the measurements are made precisely at the focus. On the other hand Gans[2] assumed the rays meeting at the focus to be incoherent—an assumption

[1] I. R. Rao, *Ind. Journ. Phys.*, 1927, **2**, 72.
[2] R. Gans, *Physik. Zeits.*, 1927, **28**, 661.

obviously not justifiable—and derived the formula

$$\rho = \rho_0 + \tfrac{1}{2} \sin^2 \theta = \rho_0 + \frac{\theta^2}{2}$$

where ρ_0 = depolarisation with parallel unpolarised light
and ρ = observed value of the depolarisation when the incident beam has a semi-convergence θ.

Cabannes[3] has discussed these rival views in his book and attempted to reconcile them, but the question has remained unsettled and somewhat obscure.

2. Case of two Intersecting Parallel Beams.

To elucidate the points at issue it is desirable to treat at first a relatively simple case.

Consider a pair of parallel, coplanar, plane polarised beams crossing each other at an angle 2θ. Let the electric vector in the beams be in the plane of the paper which is supposed to be the xy-plane. The region over which the two beams are superposed will be an interference field, the interference maxima and minima being bands parallel to the x-axis, occurring with a regular periodicity $\frac{\lambda}{4 \sin \theta}$.

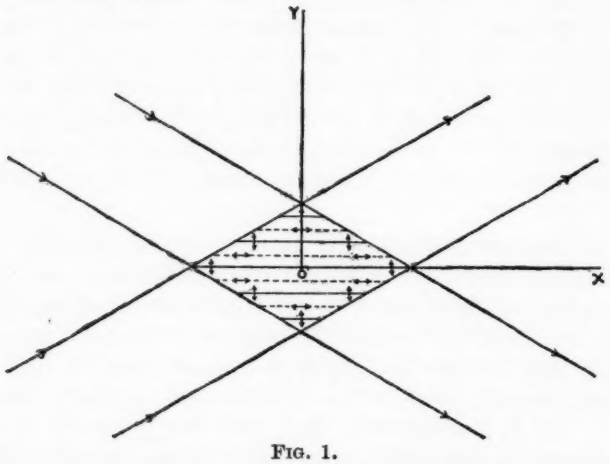

FIG. 1.

At the interference maxima (represented by thick lines in the figure), the x-components of the electric intensity annul each other so that the resultant electric vector is vertical, while the interference minima (represented by dotted lines in the figure) are places where the resultant vibration is parallel

[3] J. Cabannes, *La Diffusion Moleculaire de la Lumiere.*

to the axis of x. If the region of overlapping is occupied by molecules of a gas which scatter light in the usual way, and if one were to make observations in a direction perpendicular to the plane of the paper, *the depolarisation observed along the interference maxima will be the correct value, while at the interference minima, the electric vector being horizontal the depolarisation ratio will be reversed.* Let it now be assumed that on account of some reason, such as for instance, the lack of monochromatism in the interfering beams or the excessive closeness of the interference bands, that it is not possible to concentrate attention on the individual interference maxima. The depolarisation measured in the usual way in such circumstances would be that averaged over the whole field, due regard being had to the intensity, and would thus differ from the correct value.

At any point (x, y) in the interference field where the relative retardation between the interfering beams is $\delta = 2\ y\ \sin\theta$, the components of the electric intensity are given by

$$\left.\begin{aligned} E_x &= 2E \sin\theta.\ \sin(k\ y \sin\theta)\ \ \sin k\ (vt + y \sin\theta).\\ E_y &= 2E \cos\theta.\ \cos(k\ y \sin\theta)\ \ \cos k\ (vt + y \sin\theta).\\ E_z &= 0 \end{aligned}\right\} \quad .. \quad .. \quad (1)$$

where $k = \dfrac{2\pi}{\lambda}$

The time mean square of the components of the electric moment induced in a molecule situated at x, y are given by the equations[4]

$$\left.\begin{aligned} \overline{p_x^2} &= (A - B)\ \overline{E_x^2} + B\ (\overline{E_x^2} + \overline{E_y^2} + \overline{E_z^2})\\ \overline{p_y^2} &= (A - B)\ \overline{E_y^2} + B\ (\overline{E_x^2} + \overline{E_y^2} + \overline{E_z^2})\\ \overline{p_z^2} &= (A - B)\ \overline{E_z^2} + B\ (\overline{E_x^2} + \overline{E_y^2} + \overline{E_z^2}) \end{aligned}\right\} \quad .. \quad .. \quad (2)$$

where $A = \dfrac{1}{5}\Sigma g_1^2 + \dfrac{2}{15}\Sigma g_1 g_2$

and $B = \dfrac{1}{15}(\Sigma g_1^2 - \Sigma g_1 g_2)$

g_1, g_2, g_3, being the principal polarisabilities of the molecule.

The components of the intensity of the scattered radiation polarised parallel to the x, y and z directions will be obtained by integrating (2) over the entire field. If we call these components $\overline{P_x^2}$, $\overline{P_y^2}$, $\overline{P_z^2}$, then the depolarisation for observation in a direction perpendicular to the plane of the paper is given by

$$\rho = \frac{\overline{P_x^2}}{\overline{P_y^2}} = \frac{A \sin^2\theta + B \cos^2\theta}{B \sin^2\theta + A \cos^2\theta} = \rho_0 + \theta^2 \quad .. \quad .. \quad (3)$$

where ρ_0 is the depolarisation when $\theta = 0$.

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[4] R. Gans, *Loc. cit.*

The same result follows if the two beams are considered as incoherent and if we adopt the procedure of Gans.

3. Lens with Square Aperture.

We shall next consider the case in which a lens of focal length f limited by a square aperture of edge a is used to concentrate the light on the medium.

Let the plane of the aperture be the xy-plane and let the direction of propagation be the z-axis. Let the incident light before its passage through the lens be polarised with the electric vector parallel to the axis of x, and let the vibrations be given by $E \cos kvt$.

The components of the electric intensity at any point in the focal plane whose co-ordinates are ζ and η due to an element $dx\,dy$ of the aperture whose co-ordinates are x, y, z are given by[5]

$$\left.\begin{aligned} E_x &= -\frac{1}{\lambda f} E \cos\phi . \sin k\left(vt - f + \frac{x\zeta + y\eta}{f}\right) dx\,dy \\ E_y &= 0 \\ E_z &= -\frac{1}{\lambda f} E \sin\phi . \sin k\left(vt - f + \frac{x\zeta + y\eta}{f}\right) dx\,dy \end{aligned}\right\} \quad .. \quad (4)$$

where ϕ is the inclination of the electric vector in the ray from the element with the axis of x.

As a first approximation we may put

$$\cos\phi = 1 \text{ and } \sin\phi = \frac{x}{f}$$

The components of the electric intensity at M due to the whole aperture are obtained by integrating (4) over the entire aperture. They are

$$\left.\begin{aligned} E_x &= -\frac{E}{\lambda f} a^2 \sin k\,(vt - f)\left[\frac{\sin u}{u} \cdot \frac{\sin v}{v}\right] \\ E_y &= 0 \\ E_z &= -\frac{E}{\lambda f^2}\frac{a^3}{2} \cos k\,(vt - f).\left[\frac{\sin v}{v}\right]\left[\frac{\sin u}{u^2} - \frac{\cos u}{u}\right] \end{aligned}\right\} \quad .. \quad (5)$$

where $u = \dfrac{\pi a \zeta}{f\lambda}$ and $v = \dfrac{\pi a \eta}{f\lambda}$

Substituting these values of E_x, E_y, E_z, in equations (2) of the preceding section, and following the same treatment we get, after putting $\frac{a}{f} = 2\theta$

$$\left.\begin{aligned} \overline{P_x^2} &= \int_{-\infty}^{+\infty}\int (A\,\overline{E_x^2} + B\,\overline{E_z^2})\,d\zeta\,d\eta = \tfrac{1}{2} E^2 a^2 [A + B\tfrac{1}{3}\theta^2] \\ \overline{P_y^2} &= \int_{-\infty}^{+\infty}\int (B\,\overline{E_x^2} + B\,\overline{E_z^2})\,d\zeta\,d\eta = \tfrac{1}{2} E^2 a^2 [B + B\tfrac{1}{3}\theta^2] \\ \overline{P_z^2} &= \int_{-\infty}^{+\infty}\int (B\,\overline{E_x^2} + A\,\overline{E_z^2})\,d\zeta\,d\eta = \tfrac{1}{2} E^2 a^2 [B + A\tfrac{1}{3}\theta^2] \end{aligned}\right\} \quad .. \quad (6)$$

[5] See Lord Rayleigh, *Scientific Papers*, Vol. III, p. 80.

From these it follows that the depolarisation of the light scattered in the direction Oy is given by

$$\rho_v = \frac{\overline{P_z^2}}{\overline{P_x^2}} = \rho_{v_0} + \tfrac{1}{3}\theta^2 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (7)$$

where ρ_{v_0} is the value of ρ_v for $\theta = 0$.

If observations are made in the direction Ox, we have

$$\rho_h = \frac{\overline{P_z^2}}{\overline{P_y^2}} = 1 + \frac{1}{\rho_{v_0}} \tfrac{1}{3}\theta^2 \quad .. \quad .. \quad .. \quad .. \quad (8)$$

If the incident light is unpolarised, it is easily seen that the depolarisation of the transversely scattered light is given by

$$\rho_u = \rho_{u_0} + \tfrac{3}{8}\theta^2 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (9)$$

From (7) and (9) it follows that so far as convergence error is concerned, no advantage is gained by using light polarised with the electric vector vertical in place of unpolarised light, since ρ_{v_0} is nearly half of ρ_{u_0}. From (8) we see that when the incident light is polarised with the electric vector horizontal, the effect of convergence is to make the horizontal component appear brighter than the vertical and this effect becomes all the more striking when the value of the depolarisation is very small. Formulæ (7), (8) and (9) also follow readily if the incident beam is treated as incoherent, and if we adopt the method of Gans. What actually takes place is that the finite width of the source such as the sun, for instance, produces a mixing up of the diffraction patterns due to the different points of the source so that the ultimate effect is the same as though the rays from any single point are incoherent.

4. *Lens with Circular Aperture.*

We now go to consider the case of greater practical interest and importance, namely, the case in which the condensing lens is limited by a circular aperture of radius R.

We follow the treatment already given for the square aperture. Putting $\frac{k\zeta}{f} = p$ and $\frac{k\eta}{f} = q$, and noting that the form of the aperture is symmetrical with respect to the axes of x and y, the expressions for the electric intensity at any point in the focal plane may be written in the form

$$\left.\begin{aligned} \mathrm{E}_x &= -\frac{\mathrm{E}}{\lambda f} \sin k(vt - f) \iint \cos px \cos qy \, dx \, dy \\ \mathrm{E}_y &= 0 \\ \mathrm{E}_z &= \frac{\mathrm{E}}{\lambda f^2} \cos k(vt - f) \frac{d}{dp}\left[\iint \cos px \cos qy \, dx \, dy\right] \end{aligned}\right\} \quad .. \quad (10)$$

When the convergence of the incident beam is not too great, it is justifiable as a first approximation to assume that the x-component of the electric intensity is symmetrical with respect to the focal point $p = 0$, $q = 0$. It is thus sufficient to determine E_x along the axis of p, and so the integral in (10)

reduces to the usual diffraction integral in the case of the circular aperture. We thus obtain for the time mean square of E_x, E_y and E_z

$$\left.\begin{aligned} \overline{E_x^2} &= \frac{E^2}{2\lambda^2 f^2}\left[\pi R^2 \frac{2J_1\left(\frac{2\pi Rr}{f\lambda}\right)}{\left(\frac{2\pi Rr}{f\lambda}\right)}\right]^2 \\ \overline{E_y^2} &= 0 \\ \overline{E_z^2} &= \frac{E^2}{2\lambda^2 f^4}\left[\frac{d}{dp}\left\{\pi R^2 \frac{2J_1\left(\frac{2\pi Rr}{f\lambda}\right)}{\left(\frac{2\pi Rr}{f\lambda}\right)}\right\}\right]^2 \end{aligned}\right\} \quad .. \quad .. \quad (11)$$

where r is the distance of the point in the focal plane under consideration from the focus $p=0$, $q=0$.

It is readily shown that

$$\int_{-\infty}^{+\infty}\int \overline{E_x^2}\, d\zeta d\eta = \frac{E^2}{2}\pi R^2 2\int_0^\infty z^{-1} J_1^2(z)\, dz = \frac{E^2}{2}\pi R^2 \quad .. \quad (12)$$

and

$$\int_{-\infty}^{+\infty}\int \overline{E_z^2}\, d\zeta d\eta = \frac{E^2}{2}\pi R^2 \frac{R^2}{f^2}\int_0^\infty z^{-1} J_2^2(z) dz = \frac{E^2}{2}\pi R^2 \tfrac{1}{4}\theta^2 \quad .. \quad (13)$$

where $z = \dfrac{2\pi Rr}{f\lambda}$ and $\theta = \dfrac{R}{f}$.

Proceeding to find $\overline{P_x^2}$, $\overline{P_y^2}$ and $\overline{P_z^2}$, as in the case of the square aperture we obtain,

$$\left.\begin{aligned} \rho_v &= \rho_{v_0} + \tfrac{1}{4}\theta^2 \\ \rho_h &= 1 + \frac{1}{\rho_{v_0}}\tfrac{1}{4}\theta^2 \\ \rho_u &= \rho_{u_0} + \tfrac{1}{2}\theta^2 \end{aligned}\right\} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (14)$$

The last of the results (14) has been worked out by Gans using the idea of incoherence, while the first two which relate to the cases in which the incident light is plane-polarised can be obtained by adopting the same procedure. The significance of (14) has been already explained in section (3).

5. Remarks on the Foregoing Results.

The above investigation relates to the focal plane and assumes that the lens is uniformly illuminated and that every part of the aperture is equally effective at any given point in the focal plane where there is any appreciable intensity. This requires the use of a lens which is optically perfect. Whether it is so or not can be determined by the well-known knife-edge test. Sunlight reflected by a heliostat is allowed to illumine the entire aperture of the lens, and the rays diverging from the focus are allowed to fall on a distant screen. A sharp razor-blade is slowly made to advance through the focal

plane and the illumination of the circular patch of light on the screen is watched. If the lens is optically good, the illumination of the entire area fades off quite regularly and uniformly, so that by merely looking at the screen it is impossible to find out from which side the knife-edge is cutting across. Actual experiment with a high-class photographic lens shows that even for a quite appreciable distance on either side of the focal plane, the knife-edge test gives the same result, and within this region, the theoretical results as regards the magnitude of the convergence correction would be expected to be very nearly valid. As the extent of this region is quite comparable with the dimensions of the track over which one concentrates in practice in depolarisation work, the theoretical correction can be safely applied to the observed value so long as the lens used in the experiment is optically good, and observations are restricted to the vicinity of the focus. When we deviate far too much from the focal plane, the knife-edge test reveals a decided asymmetry in the illumination at any point, which is shown by the definite appearance of the shadow of the knife-edge marching across the illuminated area on the screen. Under such circumstances the validity of the theoretical treatment would no longer hold good, and the magnitude of the correction at any point will depend upon whether it receives illumination from the central or marginal portions of the lens. The actual correction will be smaller than the theoretical value in the former case, and larger in the latter, and the observed depolarisation of the transversely scattered light will thus vary from point to point within the visible track of the illuminating beam within the medium.

So far the necessity for the use of an optically perfect lens has been stressed as a necessary consequence of the theoretical considerations, and this evidently implies that it is also of the highest importance to have the rest of the optical parts as perfect as possible. If sunlight is employed for depolarisation work, it is essential to use a good heliostat mirror to reflect the light into the observation chamber. To avoid distortion of the incident beam as it enters the vessel containing the scattering medium, it is essential to use a flat window. The use of a bulb is highly unsatisfactory in this respect. It is desirable also that the window through which the scattered track is viewed should be free from optical defects.

6. *Some Experimental Results.*

It has been already remarked that the convergence error becomes very important when the genuine depolarisation of the substance under investigation is very small. This at once suggests that gases and vapours of small depolarisation as well as liquids and liquid mixtures near the critical point are the media in which the depolarisation would be expected to be most

susceptible to the change in convergence of the incident beam. From a practical point of view, however, the intensity of scattering is a very important factor in the experimental investigation of the question, since the accurate determination of the depolarisation over a wide range of convergence is feasible only if the intensity of scattering is relatively large.

(*a*) *Gases.*—Isobutane seemed to be favourable in the case of gases, as its depolarisation is very small, while the scattering is at the same time relatively intense. The gas was taken from a cylinder supplied by the Ohio Chemical Works, and was guaranteed to be 99% pure. The depolarisation was determined independently using two different arrangements.

(1) The gas was contained in a pear-shaped bulb of the type used by Ramanathan and I. R. Rao in their investigations, but with the addition of a projecting tube with flat window on the observation end. Sunlight reflected by a Foucault heliostat was concentrated at the centre of the bulb using a high class condensing lens in combination with an adjustable iris diaphragm, and the depolarisation of the transversely scattered light was measured in the usual way. The angle of convergence of the incident beam was determined by measuring the diameter of the illuminated area on a screen placed at a distance of one metre from the focus. The results are given in the table below :—

TABLE I.

Convergence of the incident beam $= 2\theta$	Observed value of the depolarisation $= \rho_u$	Correction $= \frac{\theta^2}{2}$	Corrected value of the depolarisation $= \rho_{u_0} = \rho_u - \frac{\theta^2}{2}$
Deg. Radian			
29° 48′ =0·520	4·04%	3·38%	0·66%
19° 48′ =0·346	2·27%	1·45%	0·82%
9° 54′ =0·173	1·06%	0·37%	0·69%

Mean value=0·72%

The values in the last column show that, in spite of the large value of the observed depolarisation when the convergence of the incident beam is large, the corrected value comes out to be very nearly the same as that for small values of convergence.

(2) The gas was contained in a cross made of pyrex glass with fused-on end plates and suitable diaphragms. A Dallmeyer photographic lens of

focal length 1 foot and adjustable aperture was used for concentrating the sunlight at the centre of the cross. The optics of the whole arrangement was thus much superior to that used in the first case. The results are recorded in the table below.

TABLE II.

Aperture	ρ_u	$\frac{\theta^2}{2}$	$\rho_{u_0} = \rho_u - \frac{\theta^2}{2}$
F/5·6	0·83%	0·4%	0·43%
F/11	0·58%	0·1%	0·48%

Mean value = 0.46%

The difference in the values of the depolarisation measured with the bulb and with the cross, emphasises the necessity for the perfection of the optical parts used in depolarisation work.

(*b*) *Liquids.*—A critical mixture of methyl alcohol and hexane distilled and sealed in a spherical bulb was found to be specially suited for the study of the convergence correction in the case of liquids, because of the close proximity of its critical temperature (29° C.) to the room temperature. The mixture was warmed just above the critical point of complete miscibility and was placed in the path of the incident beam in such a way that the centre of the bulb coincided with the focus. The use of a spherical bulb as stated above eliminates the alteration in the convergence of the track which would otherwise require to be considered. The observed and corrected values of the depolarisation are given below.

TABLE III.

2θ		ρ_u	$\frac{\theta^2}{2}$	$\rho_{u_0} = \rho_u - \frac{\theta^2}{2}$
Deg.	Radian			
28° 20′	=0·4945	3·34%	3·05%	0·29%
18° 11′	=0·3173	1·49%	1·26%	0·23%
4° 35′	=0·08	0·44%	0·08%	0·36%

Mean value = 0·29%

The observation of the Tyndall cone through a nicol in the case of the liquid mixture reveals certain interesting features which illustrate the

theoretical discussion contained in section (5). Using an incident beam of large convergence, when the nicol through which the transversely scattered light is viewed is rotated so as to transmit only the horizontal component, one finds a dark region in the middle of the Tyndall cone on either side of the focus, while the margins appear as a pair of bright streamers (Fig. 3 in the Plate). A slight rotation of the nicol either way makes the luminous cone asymmetric, the intensity fading off rapidly from one edge to the other (Figs. 2 and 4 in the Plate). The explanation for these appearances is almost self-evident in view of what has been stated in section (5). Fig. 3 in the Plate brings out in a picturesque fashion the whole mechanism of the convergence error. The dark centre shows how the genuine depolarisation is exceedingly small, and how the greater part of the illumination observed at the focus is contributed by the marginal portions of the lens.

In conclusion, it is my greatest pleasure to record my respectful thanks to Professor Sir C. V. Raman, for suggesting the present investigation, and for much valuable guidance and criticism in the course of the work.

7. *Summary.*

The scattering of light in an interference field is discussed, and it is shown that for the simple case of two parallel plane-polarised intersecting beams, the depolarisation at the interference maxima gives the correct value, while at the interference minima the depolarisation ratio is reversed. The average of the depolarisation taken over the whole field is higher than the correct value. The treatment is extended to the cases in which a lens covered with a square aperture, and with a circular aperture, respectively, is used to concentrate the light on the scattering medium. It is shown that the observed values of the depolarisation would deviate from the genuine values by a correction factor which involves the square of the angle of convergence. The observed depolarisation ρ is given by

$$\rho_v = \rho_{v_0} + a\theta^2$$

$$\rho_h = 1 + \frac{1}{\rho_{v_0}} a\theta^2$$

$$\rho_u = \rho_{u_0} + 2a\theta^2$$

where a has the value $\frac{1}{3}$ for a square aperture, and $\frac{1}{4}$ for a circular one. The subscripts v, h, u refer to the cases in which the incident light has its electric vector vertical, horizontal and is unpolarised respectively. It is pointed out that the same results follow by treating the incident beam as a bundle of incoherent rays. Some consequences of the theoretical results are discussed and the necessity for the perfection of the optical parts used in depolarisation work is emphasised. Experimental results are given which illustrate the points discussed in the paper.

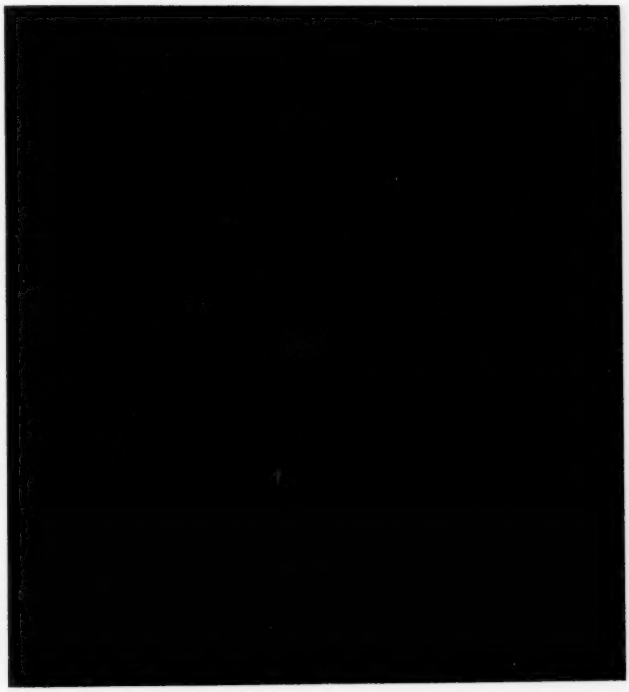

FIG. 2.

FIG. 3.

FIG. 4.

THE DYNAMICAL THEORY OF THE DIAMOND LATTICE.

Part III. The Diamond-Graphite Transformation.

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1. Introduction.

It is common knowledge that diamond is spontaneously transformed to graphite or black carbon at high temperatures. There have been many investigations to find out whether the transformed substance is really graphite or contains any other modification of carbon and to determine the exact temperature of transformation of diamond. That the transformed substance consists of minute crystals of graphite has been established by two Hungarian investigators Emerich Szarvasy and Béla Lányi.[1] They found that the transformation was rapid at 1760° C. but unchanged diamond was still present. On Röntgen examination, they found that the relative intensities of the stronger graphite lines are the same in natural or artificial Acheson graphite and in graphite formed from diamond by graphitization. The size of the sub-microscopic crystals of graphite formed from diamond at 2000° C. was about the same as those of graphite produced from methane. G. Friedel and G. Ribaud[2] who have studied the weak birefringence in diamond have also studied the transformation of diamond to graphite and they find the temperature of transformation to be 1885° C. P. Libeau and M. Picon[3] have also studied the transformation with their technique of high temperature heating and they place the temperature of the rapid transformation at about 2000° C. At lower temperatures they find that the transformed substance consists not only of graphite but also of black diamond which gives the same X-ray pattern[4] as diamond itself. M. de Kay Thompson and P. K. Frölich[5] have also studied the conversion of diamond to graphite

[1] Emerich Szarvasy and Béla Lányi, *Math. Naturw. Anz. Ungar. Akad. Wiss.*, 1931, **48**, 137.

[2] G. Friedel and G. Ribaud, *Comptes Rendus*, 1924, **178**, 1126.

[3] P. Libeau and M. Picon, *Comptes Rendus*, 1924, **179**, 1059.

[4] W. Gerlach, *Zeit. f. Anorg. und Alg. Chemie*, 1924, **137**, 331.

[5] M. de Kay Thompson and Per K. Frölich, *Trans. Amer. Electro-chem. Soc.*, 1923, **43**, 161.

at various temperatures for various times of heating confirming that the transformed substance is graphite by Brodie's Test. They place the temperature of slow transformation at 1650° C. and rapid transformation at 1750° C. and remark that diamonds turn black at 1200° C. due to the numerous cracks causing the absorption of light by total reflection. If this explanation is genuine, it seems to offer also an explanation for the blackening noticed by P. Libeau and M. Picon at such temperatures. The conclusion of Vogel and Tamman[6] who have studied the conversion of diamond, that diamond starts converting to graphite at 1000° C. appears to require modification in the light of the remark of M. de Kay Thompson and P. K. Frölich. There are many others who have studied the transformation from the time of Francis I who burnt a portion of diamond at the focus of a large concave mirror. Among them are Jacquelain,[7] v. Schrötter,[8] Moisson,[9] Rose[10] and Hon. C. A. Parsons and A. A. C. Swinton.[11]

The purpose of this paper is to explain as to how the graphite structure can be derived from that of diamond by a simple transformation and also to calculate the temperature at which diamond transforms to graphite. The calculated temperature is in satisfactory agreement with the experimental determinations. The ideas followed up here seem to be not very special to the diamond-graphite transformation itself but can have extensions for similar types of transformation of other substances.

2. *The Diamond-Graphite Transformation.*

It has been shown by X-ray analysis that the diamond structure[12, 13] is made up of two cubic face-centred lattices interpenetrating one another in a manner such that an atom of one lattice is equally nearest to four atoms of the other lattice, the C-C distance being 1·54 Å and the edge of the unit cubic cell being 3·56 Å. Bernal,[14] Hassel and Mark[15] and others have shown that the graphite structure is made up of series of parallel plane equidistant layers of carbon atoms and that each layer is a hexagonal net of atoms such that half the atoms in a layer lie directly along the lines parallel to the c-axis through half the atoms of *both* the adjacent layers and the other half lie along

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[6] R. Vogel and G. Tamman, *Zeit. f. Phy. Chemie*, 1910, **69**, 598.
[7] Jacquelain, *Ann. d. Chim. et Phy.*, 1847, **20**, 468.
[8] A. R. v. Schrötter, *Sitzungsber. Akad. Wiss. (Wien)*, 1871, **63**, 465.
[9] H. Moisson, *The Electric Furnace*; *Comptes Rendus*, 1893, **117**, 423.
[10] G. Rose, *Monatsber. Berliner Akad.*, 1872, p. 685.
[11] Hon. C. A. Parsons and A. A. C. Swinton, *Proc. Roy. Soc. (A)*, 1907, **80**, 184.
[12] W. H. Bragg and W. L. Bragg, *Proc. Roy. Soc. (A)*, 1913, **89**, 27.
[13] W. Ehrenberg, *Zeit. f. Kristall.*, 1926, **63**, 320.
[14] J. D. Bernal, *Proc. Roy. Soc. (A)*, 1924, **106**, 749.
[15] O. Hassel and H. Mark, *Zeit. f. Phy.*, 1924, **25**, 317.

the lines parallel to the c-axis through the centres of the hexagons of the adjacent layers, the C-C distance being 1·42 Å and the distance between the layers being 3·41 Å. Knowing the above structures of diamond and graphite, one can now raise a very natural and important question as to how we can derive the graphite structure from the diamond structure. In the following we have proposed a solution for the above question and have calculated the temperature at which diamond converts to graphite, which agrees well with the experimental determinations of the said temperature.

In Part I,[16] it has been pointed out by the author that the vibration of the two cubic face-centred lattices of diamond is Raman-active but infra-red inactive and that it has the frequency 1332 cm.$^{-1}$ We now seek the origin for the conversion of diamond to graphite in the above vibration which is triply degenerate. When the temperature of the crystal is raised or when its internal energy is increased, the amplitude of the vibration increases. At a definite increase of the amplitude, we will show in the following that the instability of diamond sets in. We will first give the purely geometrical aspect of the problem and then present its physical aspect in which we have followed a method for calculating the temperature at which the lattice vibration is of sufficient amplitude to favour the diamond-graphite transformation.

3. *The Geometrical Aspect of the Transformation.*

In the following we will show that the diamond structure can be transformed to a graphite-like structure by the following elementary operations:—

(*a*) A definite displacement of the two cubic face-centred lattices of diamond relative to one another along a particular direction (Figs. 1 and 2).

(*b*) A definite homogeneous dilatation of the whole crystal along the same direction (Fig. 3).

(*c*) A definite homogeneous gliding of the planes obtained by the above two transformations perpendicular to the same direction (Fig. 4.)

(*a*) If we displace the two cubic face-centred lattices of diamond relative to one another along a diagonal of the unit cubic cell by 1/12 the length of the diagonal or increase the length of the C-C bonds parallel to the diagonal by a third of it, we get a structure which resembles apparently the graphite structure and which we call it as the α-pseudo-graphite structure. The following are its properties:—

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[16] N. S. Nagendra Nath, *Proc. Ind. Akad. Sci.* (*A*), 1934, 1, 333.

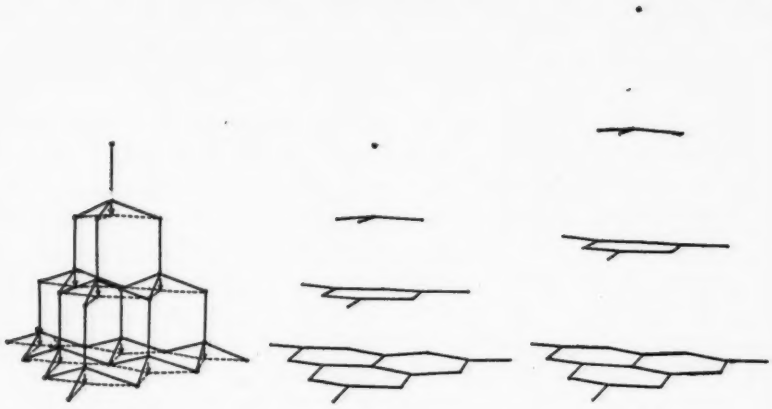
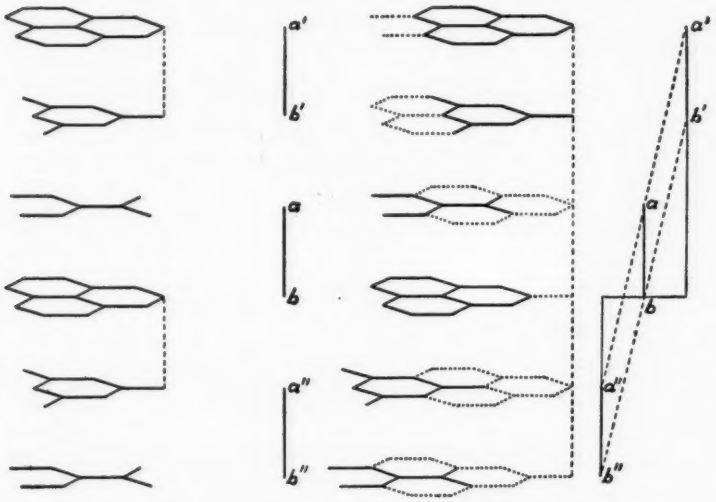


FIG. 1. FIG. 2. FIG. 3.

FIG. 1—Diamond structure→ α-pseudo-graphite structure.
FIG. 2—α-pseudo-graphite structure.
FIG. 3—β-pseudo-graphite structure.



β-pseudo-graphite structure. Graphite structure.

FIG. 4.

(1) The α-pseudo-graphite structure is similar to the graphite structure in that it is made up of equidistant parallel plane layers of carbon atoms, each layer being a hexagonal net. But half the atoms in a layer A are directly along the normals to the planes through half the atoms of only one

of the adjacent layers B and the same set of half the atoms in A are directly along the normals to the planes through the centres of the hexagons of the remaining adjacent layer C ; the remaining set of half the atoms in the layer A will be directly along the normals to the planes through half the atoms in the layer C and the same atoms in A will be directly along the normals through the centres of the hexagons in B.

(2) Assuming the C-C distance in diamond to be 1·54 Å, we can easily calculate the C–C distance in a plane of the α-pseudo-graphite structure. It is $1{\cdot}54 \sin [\cos^{-1}(-\frac{1}{3})]$ Å $= 1{\cdot}54 \times 2\sqrt{\frac{2}{3}}$ Å $= 1{\cdot}45$ Å. This agrees pretty closely with 1·42 Å in graphite determined by X-ray analysis.

(3) The distance between the plane layers in the α-pseudo-graphite structure is (1·54 + 1·54/3) Å or 2·05 Å while it is 3·41 Å in graphite.

(*b*) This transformation is only a simple homogeneous dilatation of the α-pseudo-graphite structure along a normal to its planes by the ratio 3·41/2·05 or 1·66. We will call the transformed structure after the above operation as the β-pseudo-graphite structure which is practically identical with the graphite structure in the C–C distance, the distance between the layers and the structure of atoms in each layer except the symmetry of the planes taken as a whole. For example, every plane is a plane of reflection in the case of the graphite structure while it is not so in the case of the α- or β-pseudo-graphite structures. The next process to be described consists in transforming the β-pseudo-graphite structure into the graphite structure.

(*c*) The successive plane layers in the β-graphite structure may be symbolically represented by

$$\ldots A\ B\ C\ A\ B\ C \ldots$$

and those in graphite may be represented by

$$\ldots A\ B\ A\ B\ A\ B \ldots$$

where all the atoms in any of the planes A, B, C cannot be superposed on the atoms of any one of the remaining by the motion of the plane along a normal to the parallel planes. This is obvious in virtue of the property (1) in (*a*).

The required transformation of the β-graphite structure to the graphite structure is accomplished by considering a particular kind of gliding motion of the planes of the β-graphite structure. It consists in moving all the planes along a C–C direction lying in the planes with two adjacent planes as a rigid unit such that an unit suffers relative displacements with its adjacent units, which are equal in magnitude to the C–C distance but are opposite in sign. A clear pictorial representation of the transformation is given in the preceding figures.

4. The Physical Aspect of the Transformation.

It is clear from the above that there exists a simple continuous process by which we can derive the graphite structure from that of diamond. We shall now discuss its bearing on the physical aspect of the transformation.

We know that both diamond and graphite are normally stable substances. The stability of a crystal implies that the energy of the normal configuration is a minimum for all infinitesimal displacements of the lattice. With this idea in view, let us now discuss the course of the energy curve during the diamond-graphite transformation. While discussing it, *we ignore the forces between the layers in graphite as they are, we hope, exceedingly feeble compared to the valence forces in the planes.* As the process starts from diamond, the energy of the lattice increases in accordance with the fact that the energy of normal diamond is minimum for all infinitesimal displacements of the lattice. Similarly, starting from graphite to diamond the energy of the lattice also increases. As the process under consideration is a continuous one, the above means the existence of at least one stage at which the energy of the lattice is maximum, *i.e.*, a stage at which the energy of the lattice no longer increases either from the diamond side or the graphite side. But there cannot be more than one such stage or else it would imply the existence of minima of energy or of stable configurations in between the maxima distinct from those of diamond or graphite which seems to be highly physically improbable. In other words, the above considerations mean that there exists a single finite potential barrier between the diamond and the graphite states. We will call the stage of the lattice having the energy of the peak of the barrier as the α-stage.

If we now increase the thermal energy of diamond which is exhibited as the vibrational energy of its atoms, to such an extent that it will have the energy of the α-stage, the immediate instability of diamond will set in. Since diamond requires a definite temperature to possess a definite heat content from the thermal point of view, we can calculate the temperature at which diamond becomes unstable if we know the energy of the lattice at the α-stage.

The next question will be as to how to plot the energy curve during the process of transformation quantitatively. It appears to be exceedingly difficult to give even a fairly reasonable answer to this question. But we make here an approximation which will not be perhaps far from the truth. We know from molecular spectra that the course of the potential energy curve of a diatomic molecule is given for a fair approximation by a Morse function. In the case of diamond, we will assume a Morse function characterised by the constants D and a for all the chemical bonds in it. As the

Morse function is generally valid for fairly large variations of the internuclear distance of a diatomic molecule, we can assume the Morse function of the C–C bonds in diamond to be valid so long as diamond is stable. That is, the Morse function of the C–C bonds in diamond may be regarded as valid till the α-stage. To get an approximate function for the energy curve between the α-stage and the graphite state, we think of the transformation of the graphite structure to that of diamond. Regarding the C–C bonds in the layers of graphite to be all identical in character so far as our calculations are concerned here, we assume a Morse function characterised by the constants D' and a' for all the C–C bonds in graphite and also assume that it is valid between the graphite state and the α-stage. One may say that our approximation is weak in this case for we have ignored the forces between the layers. It is no doubt a defect, but it is one which cannot be remedied immediately and justifiably. However, we believe a part of the defect is compensated for in our assumption that the C–C bonds in the planes of the graphite structure will have the same character till the α-stage instead of the fact that there is a gradual weakening of the C–C bonds in the planes and the gradual appearance of the C–C bonds perpendicular to the planes.

The dissociation energy D of a normal C–C bond[17] is 72·6 K. cal./gm. mol. We know from the data on the Raman spectra of organic compounds that the force constant of the C–C bond is in the neighbourhood of about 4×10^5 dyn./cm., the expression for the force constant from the Morse formula being $2Da^2/N$. From this, it follows that a is $\eqsim 2\times10^8$. Now we can regard the dissociation energy of a C–C bond in graphite to be $1\frac{1}{3}$ times that in diamond for it is observed by Roth[18] and his collaborators that the heats of combustion of diamond and graphite are practically identical. So D' is 96·8 K. cal./gm. mol. We now assume that the force constant of a C–C bond in graphite is about $1\frac{1}{3}$ times that in diamond. To this assumption, we attach no physical significance whatsoever; we are only aiming at an approximate value of the force constant of a C–C bond in graphite. With this assumption $a' \eqsim 2\times10^8$.

Let r' be the internuclear distance of the C–C bonds parallel to the line of displacement and r be the internuclear distance of the other C–C bonds

[17] K. Fajans, *Ber. der Deut. Chem. Ges.*, 1920, **53**, 643; 1922, **55**, 2826.
Prof. K. Fajans gives the values 75 K.cal./gm. mol. and 100 K. cal./gm. mol. for D and D′ respectively. The value 72·6 K. cal./gm. mol. for D has been taken from the work of Prof. E. Hückel. This difference does not affect our calculations in this paper to any appreciable extent.

[18] W. A. Roth and H. Wallasch, *Ber. der Deut. Chem. Ges.*, 1913, **46** (1), 896.
W. A. Roth, *Zeit. f. Electrochem.*, 1915, **21**, 3.
W. A. Roth and G. Naeser, *Zeit. f. Electrochem.*, 1925, **31**, 461.

equally inclined to the line of displacement. As we proceed from the diamond state to the a-stage r' is a definite function of r as there is only one co-ordinate during that interval.

If E_a corresponds to the energy gained by a gram-atom of the diamond lattice when it comes to the a-stage,

$$E_a = \frac{D}{2}\left[\left\{1-e^{-2(r'_a-1\cdot54)}\right\}^2 + 3\left\{1-e^{-2(r_a-1\cdot54)}\right\}^2\right]$$

$$= \frac{3D'}{2}\left\{1-e^{-2(r_a-1\cdot42)}\right\}^2 \qquad (1)$$

where $2D$ and $3D'/2$ are the dissociation energies of gram-atoms of diamond and graphite respectively and r's are given in Ångstrom units and their values at the a-stage are denoted by the subscript a. Solving the equation (1), we find

$$r'_a = 1\cdot68 \text{ Å} \quad \text{and} \quad r_a = 1\cdot50 \text{ Å}.$$

Hence the a-stage in the process of the transformation occurs when the two cubic face-centred lattices are displaced apart along a diagonal of the unit cell by $(1\cdot68-1\cdot54)$ Å or $0\cdot14$ Å. We also find

$$E_a = 2920 \text{ cals./gm. atom.}$$

The potential energy curve of the transformation is drawn in Fig. 5.

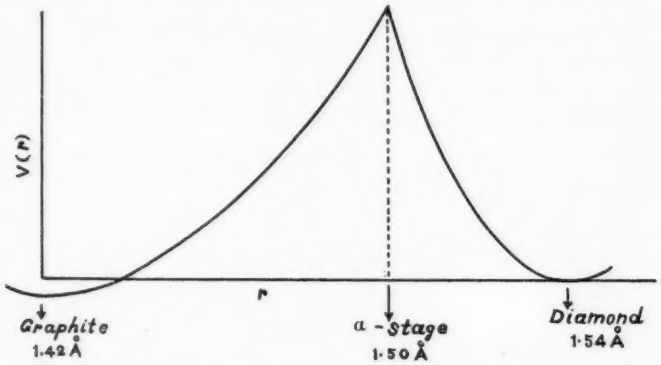


FIG. 5—The potential energy curve between the diamond and the graphite states as a function of r. The initial energy of the diamond lattice is taken as zero.

The above calculations mean that the diamond lattice will only be stable if the change in the C–C distance parallel to the line of displacement does not exceed $0\cdot14$ Å. So, if we increase the thermal energy of diamond which is exhibited as the vibrational energy of its atoms to such an extent that the lattice vibration will have an amplitude of $0\cdot14$ Å, the instability

of diamond will set in. Since the lattice vibration is triply degenerate, the maximum heat content of diamond without its being unstable is $2920 \times 3 = 8760$ calories/gm. atom. We make now a calculation of the temperature at which the instability of diamond will set in and at which diamond will have the maximum heat content.

Using the Einstein formula for the heat content, we get

$$\frac{3\,R\,\Theta}{\exp(\Theta/T) - 1} = 8760 \qquad (2)$$

where $\Theta = h\nu/k$, where the frequency ν corresponds to the characteristic frequency expressed in absolute units. If we assume that the characteristic Einstein frequency of diamond has a magnitude equal to the Raman frequency 1332 cm.$^{-1}$ (in wave numbers), we get $\Theta = 1907$. Solving (2), we get

$$T \eqsim 2290 \text{ A.}$$
$$\eqsim 2000^\circ \text{ C.}$$

The temperature T may also be calculated by the use of the Nernst-Lindemann formula for the heat content of a crystal, which gives satisfactory results for the specific heat of diamond at higher temperatures. According to it

$$\frac{3}{2}R\left[\frac{\Theta}{\exp(\Theta/T) - 1} + \frac{\Theta/2}{\exp(\Theta/2T) - 1}\right] = 8760 \qquad (3)$$

where the value for Θ is 1940 as given by Nernst and Lindemann[19] themselves. Solving the equation (3), we get

$$T \eqsim 2110 \text{ A.}$$
$$\eqsim 1850^\circ \text{ C.}$$

These calculations of the temperature at which diamond converts to graphite stand in good agreement with the experimental determinations which lie between 1650° C. and 1885° C., the temperature of rapid transformation being about 1750° C. according to M. de Kay Thompson and P. K. Frölich and Emerich Szarvasy and Béla Lányi.

The author is highly thankful to his professor Sir C. V. Raman for his great and helpful interest in this work.

5. *Summary.*

The transformation of the diamond structure to the graphite structure is explained in terms of three elementary operations, one of which is a definite displacement of the two cubic face-centred lattices of diamond relative to one another. It is shown here that for a certain displacement of the

[19] W. Nernst and F. A. Lindemann, *Ber. Berliner Akad.*, 1911, 1, 494; *Zeit. f. Electrochem.*, 1911, 17, 817.

component lattices, diamond attains maximum energy of its configuration and becomes unstable. The temperature at which diamond becomes unstable and transforms to graphite is calculated and is shown to be in good agreement with the experimental determinations.

The ideas followed up here seem to be not very special to the diamond-graphite transformation itself but can have extensions for similar types of transformation of other substances.

Note added in proof.—While this paper was in the Press, two papers by W. Lasareff have appeared (*Jour. Phys. Chem.*, 1935, **39,** 913; *Physica*, 1935, **2,** 737) in which he has calculated the dissociation energy of a C–C bond in diamond. The value given in *Physica* is $132 \pm 3 \cdot 5$ K. cals./mol. for D, departing greatly from the values known till now which range between 70—80 K. cals. Lasareff has argued that a carbon atom in diamond is in the (^{5}S) state while a carbon atom in the gaseous state is in the (^{3}P) state and that the difference between the energies of these two states has to be considered when calculating the dissociation energy of a C–C bond in diamond by the help of the data regarding the sublimation heat. However, it should be noted that this great change in the dissociation energy of a C–C bond does not affect our calculations of E_a, as Da^2 the coefficient of the quadratic term r^2 does not vary for it is equal to NK/2 where N is the Avogadro number and K is the force constant of the C–C bond whose value has been assumed to be $\backsimeq 4 \times 10^5$ dyn./cm. Thus a change in D with the corresponding change in a affects only higher order terms. Thus our results should not be affected to a great extent by a change in D. We have made calculations of a, a', r_a, r_a' and E_a assuming Lasareff's value for D ($D' = 4D/3 = 176$ K. cal./mol.). The value of a is $1 \cdot 48 \times 10^8$ cm.$^{-1}$ and the values of r_a and r_a' are the same old values 1·50Å and 1·68Å respectively. E_a would be 3040 cals./gm. atom. It follows from the above that T is $\backsimeq$ 2080°C. according to the Einstein formula and that it is $\backsimeq$ 1900°C. according to the Nernst-Lindemann formula. These values are again in agreement with the experimental determinations.

REDETERMINATION OF THE DEPOLARISATION OF LIGHT SCATTERING IN GASES AND VAPOURS.

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1. *Introduction.*

In a previous communication to these *Proceedings*,[1] the author has discussed at length the question of the dependence of the observed value of the depolarisation on the finite convergence of the incident beam, when, as is usual in dealing with gases and vapours of small depolarisation, a condensing lens is employed to concentrate the light on the scattering medium. In view of the conclusion arrived at theoretically, and confirmed experimentally that *the depolarisation of the transversely scattered light measured at the focus is definitely higher than the genuine value*, the magnitude of the deviation depending in a perfectly determinate way on the convergence of the incident beam, it appeared to be highly important to take up a systematic redetermination of the depolarisation in the case of a number of gases and vapours because of the uncertainty that attaches to the values reported by previous experimenters who have partially or totally ignored the correction for the convergence of the incident beam. The present paper contains the results of the experimental study of more than a dozen gases and vapours. The values of the depolarisation show in many cases not only a definite departure from those reported by previous workers, but present certain new and interesting features which will be discussed in the course of the paper.

2. *Experimental Technique.*

By far the greater portion of the experimental study of the depolarisation of gases and vapours is due to the pioneer work of Lord Rayleigh in England, of Cabannes and his co-workers in France, and of Prof. Raman and his students at Calcutta. A critical review of the experimental technique of the different workers is given in Cabannes' book.[2] While Lord Rayleigh and Prof. Raman have employed metallic crosses of large capacity painted black inside, with suitable diaphragms to protect against parasitic light, Cabannes and his co-workers have mostly used smaller crosses made of glass

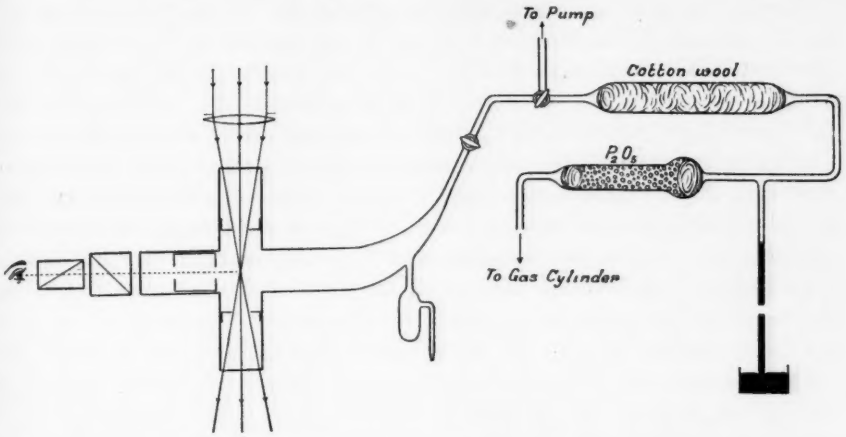
[1] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, A, 1935, **2**, 133.
[2] J. Cabannes, *La Diffusion Moleculaire de la Lumiere*, 1929.

with no diaphragms inside, and painted black externally. Although each technique has its own advantages, experience has shown the present author that the best arrangement is one in which the advantages of both the above modes of experimentation are sought to be combined. Towards this end, a cross in pyrex glass of over a litre in capacity was made with the following approximate dimensions. The tube taken was 4 cms. in diameter, and three of the four arms were about 20 cms. in length. The fourth arm opposite the observation side was much longer and was drawn out and bent up in the shape of a horn to the end of which was attached a pyrex stopcock for admission of gas into the cross. Although the use of diaphragms may not be very important when the photographic method is adopted for depolarisation measurements, accurate visual photometry is practically impossible unless the utmost precautions are taken to avoid parasitic light from entering within the field of observation. Suitable diaphragms of oxidised brass were therefore put in inside the cross. These diaphragms were made out of short lengths of thin brass tube one of the ends being closed by a thin brass plate having a central hole of $\frac{1}{2}$ inch diameter. The surfaces of the diaphragms were rendered black by immersing them in an ammoniacal solution of copper carbonate. They were then rolled in thin asbestos paper and introduced into the arms of the cross. After fixing the positions of the diaphragms within the cross by a preliminary experiment, the open ends of the three arms were closed by fusing on flat pyrex plates (previously examined between crossed nicols for strain) in the way recommended by Martin.[3] The whole cross excepting the end windows was painted dull black externally. The complete eschewal of all traces of paint from within the cross ensured perfect freedom from contamination of the gases and vapours studied.

The cross was mounted on a stool provided with levelling screws and spirit level, and observations were made within a dark cabin into which sunlight was reflected by a single mirror Foucault heliostat. A Dallmeyer photographic lens of adjustable aperture, and focal length 1 foot fixed to the wall of the cabin served to concentrate the sunlight at the centre of the cross. The whole arrangement was such as to give an exceedingly nice background against which even the faintest tracks could be seen with but little difficulty.

All the gases were taken directly from commercial cylinders supplied by the Ohio Chemical and Manufacturing Co., and were guaranteed a high degree of purity. The scheme of the experimental arrangement is shown diagrammatically in the figure. The gases were admitted into the cross at atmospheric pressure through a tube of anhydrous P_2O_5 and a long plug

[3] W. H. Martin and S. Lehrman, *Jour. Phys. Chem.*, 1922, **26**, 76.



of compressed cotton wool after evacuating the whole system by means of a Cenco Hyvac Pump. Rubber connections were avoided as far as possible to minimise leaks, and special care was taken to see that the system was perfectly leak-tight before commencing the experiments. Estimates of depolarisation were made visually by the usual Cornu method.

In the case of CCl_4, the technique adopted was slightly different. Extra-pure CCl_4, guaranteed to be free from CS_2, was refluxed with freshly distilled mercury for several hours and finally distilled at constant boiling point. A small quantity of the liquid was introduced into the bulb attached to the longer arm of the cross by means of the side tube and the latter was then sealed off. The CCl_4 was frozen in liquid air, and the cross was exhausted to the highest vacuum. The stopcock was then closed, and the liquid air bath removed. As the CCl_4 rises up to the room temperature, the vapour pressure is quite appreciable to give a scattering of sufficient intensity to make accurate measurements.

3. *Adjustments and Sources of Error.*

The accurate estimation of small depolarisation values with which one is confronted in the case of the majority of gases and vapours necessitates the utmost precautions to safeguard against various sources of error which tend to vitiate the observations. Unpolarised light diffused by the background is highly detrimental in the case of visual photometry as has been already pointed out. The error arising from this source is got rid of by the use of suitable diaphragms, and by viewing the two images of the track seen through the double image prism against the same background. Horizontality of the axis of the incident beam is very important, and is secured

by setting the cross horizontal with the spirit level. Normality of the direction of observation to the axis of the incident track is easily secured when the container is cross-shaped. The principal section of the double image prism is set vertical by viewing an illuminated plumb line, and rotating the prism about a horizontal axis till the two images are entirely superposed.

The effect of the finite convergence of the incident beam is to enhance the value of the depolarisation, and the correction to be applied to the observed value under this head is given by $\theta^2/2$, where θ is the semi-angle of convergence. It may be remarked that the experimental results of Dr. I. Ramakrishna Rao[4] and the later work of Parthasarathy[5] require correction in this direction.

4. *Results.*

The table below gives the experimental results after being corrected for the convergence of the incident beam. An aperture of F/5·6 was employed in all cases and the correction required for the observed value can be easily seen to be 0·4%.

Gas		% Purity	Depolarisation
Methane	CH_4	96·5	0·34%
Ethane	C_2H_6	90	0·50%
Propane	C_3H_8	99·9	0·66%
N. Butane	C_4H_{10}	99	0·85%
Isobutane . ..	C_4H_{10}	99	0·46%
Cyclopropane	H_2C $H_2C \triangle CH_2$	99·5	0·52%
Propylene	C_3H_6	99·5	2·91%
Methyl Chloride ..	CH_3Cl	99·5	1·95%
Ethyl Chloride	C_2H_5Cl	99·5	1·49%
Carbon Tetrachloride ..	CCl_4	..	0·15%
Dimethyl Ether ..	$CH_3 \cdot O \cdot CH_3$	99·95	1·20%
Argon	A	86	0·42%
Hydrogen Sulphide ..	H_2S	99·73	0·30%
Nitrous Oxide	N_2O	98	12·95%

[4] I. R. Rao, *Ind. Jour. Phys.*, 1927, **2**, 61.

[5] S. Parthasarathy, *Ind. Jour. Phys.*, 1932, **7**, 139.

5. *Discussion of Results.*

As has been already remarked, the results of the author are, in many cases, entirely at variance with those of previous experimenters.

Methane.—We shall commence with methane, the leading member of the paraffin series. The first outstanding result of the investigation is that the genuine depolarisation factor of methane is considerably lower than what it has been till now assumed to be. While Cabannes gave the value 1·5% and Parthasarathy 1·12%, the actual value appears to be of the order of 0·3%. Considering the fact that the residual impurities in methane are most probably some of the higher hydrocarbons whose depolarisation factors are quite small, the observed depolarisation of methane seems to be quite genuine. Thus, for instance, if we assume that the 3·5% impurity is all ethane whose intensity of scattering is roughly thrice as great as that of methane, the observed depolarisation of methane will be affected only in the second place of decimals. It is not improbable that the source of this depolarisation is to be sought for in the existence of depolarised Raman scattering. The Raman Spectrum of methane shows an intense line at 2915 cm.$^{-1}$ corresponding to the total symmetric vibration of the molecule, which according to the observations of Bhagavantam[6] is depolarised to the extent of 8%, but possesses no rotational fine structure. On the other hand, the intense band at 3022 cm.$^{-1}$ is highly depolarised to the extent of 80%, and shows equispaced rotation lines on either side of it. Stuart[7] seems to be of opinion that this strongly depolarised vibration band would be responsible for a spurious depolarisation of the Rayleigh radiation to the extent of 0·1 to 0·5%, when one is working with white light as is usual in depolarisation measurements. Thus, in the present case where sunlight was employed, the photographic lens used for focussing the beam transmits the far violet end of the spectrum, say up to 3000 Å U. and the corresponding vibration scattering would fall well within the region of greatest visibility. If this view be correct, and a filter be employed which cuts off the entire violet and blue regions of the spectrum on the incident side, and another which cuts off the entire region beyond the green and yellow be employed on the observation side, we should expect the depolarisation of methane not to differ from zero. All these considerations lend strong support to the view that the Rayleigh scattering in the case of methane is completely polarised. This conclusion is in perfect accord with the observation of Bhagavantam,[8]

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[6] S. Bhagavantam, *Nature*, 1932, **129**, 830.
[7] H. A. Stuart, *Molekulstruktur*, 1934, p. 192.
[8] S. Bhagavantam, *Nature*, 1932, **130**, 740.

later confirmed by Lewis and Houston,[9] that even prolonged exposures extending over a week fail to bring out any rotation wings for the Rayleigh line in the case of methane. The assumption of the anisotropy of the carbon atom thus appears to be definitely uncalled for to explain the depolarisation of methane. In this connection, a redetermination of the depolarisation factor of the total symmetric vibration line would be of great interest, since, as has been remarked by Stuart,[10] Bhagavantam's value appears to be too high.

Higher homologues.—The second important outcome of the experimental work is the fact that as we pass from methane to the higher homologues, the depolarisation shows a steady increase from 0·34% in the case of methane to 0·85% in the case of normal butane. Cabannes, however, arrived at the conclusion that the depolarisation does not change appreciably from one member to another, but the conclusion of the author is supported by the observations of Parthasarathy.[11] It thus appears that anisotropy is not wholly unconnected with the geometric form of the molecule. That this is so is again shown by the fact that while normal butane has a depolarisation of 0·85%, for isobutane the depolarisation drops down to 0·46%, in conformity with the greater symmetry of the molecule.

Other hydrocarbons.—Cyclopropane, whose depolarisation does not appear to have been measured by any of the previous workers, shows a very small value, which is not surprising in view of the known low depolarisation of Cyclohexane. Propylene shows a high depolarisation, as would be expected on account of the double bond.

Methyl and Ethyl chlorides.—Methyl chloride is definitely more anisotropic than ethyl chloride, contrary to the observations of Cabannes. The large increase in the value of the depolarisation which results from the substitution of one atom of hydrogen in methane by an atom of chlorine is very significant. While this observation is in qualitative agreement with the results of Parthasarathy, it is in total disagreement with those of Cabannes who finds very little change between the depolarisation factors of methane and methyl chloride.

Carbon tetrachloride.—The depolarisation of the tetrahedral molecules has remained for a long time a puzzling and unintelligible problem. For CCl_4, the depolarisation in the vapour state was estimated to be 0·77% by Cabannes, 0·5% by Ramakrishna Rao and 0·62% by Parthasarathy. Stuart[12] finds these values to be wholly incompatible with

[9] M. Lewis and W. V. Houston, *Phys. Rev.*, 1933, **44**, 903.
[10] H. A. Stuart, *loc. cit.*, p. 329.
[11] S. Parthasarathy, *loc. cit.*
[12] H. A. Stuart, *loc. cit.*, p. 193.

his measurements of the Kerr-constant of CCl_4 from which he concludes that the departure of the molecule from spherical symmetry is imperceptibly small, and would not be responsible for a depolarisation of the vapour exceeding 0·15%. The author's result stands in good agreement with this value. It should, however, be pointed out that the experimental value itself gives only an upper limit for the depolarisation, since in the actual measurements, all possible sources of error only tend to enhance the genuine value, and also because, here, one is well-nigh at the limit of accuracy in depolarisation measurements. As Stuart[13] has pointed out, the investigation of the fine structure of the Rayleigh line, as well as that of the total symmetric vibration Raman line in the case of CCl_4 vapour, would be of extreme interest in this connection.

It might on first consideration seem conceivable that a small anisotropy would be caused in the case of CCl_4 by the presence in one and the same molecule of chlorine isotopes of different masses (35 and 37). However, on account of the physical similarity of isotopes with nearly equal masses, the magnitude of this anisotropy would appear to be vanishingly small.

Argon.—The case of argon demands special explanation. In the first place, it will be noticed that the sample employed is very impure. The most probable impurity appears to be nitrogen and if it be assumed that the 14% impurity is all nitrogen, it follows from simple calculation that the depolarisation of argon is not sensibly different from zero, as the depolarisation of nitrogen is about 3%, and the relative scattering powers of argon and nitrogen are not very different.

The reality or otherwise of the depolarisation of the rare gases has been an unsettled issue. Experimentally, Cabannes appears to have found a small depolarisation of 0·5% for argon, krypton and xenon, while for neon the upper limit is given as 1%. The case of helium is again very uncertain, the upper limit for its depolarisation being given as 6·5% by Lord Rayleigh and as 3% by Parthasarathy. From the theoretical standpoint these values are difficult to comprehend. The ground state of the atoms of the rare gases is the ^1S state, and theory indicates that the scattered radiation corresponding to such terms should be linearly polarised. Placzek[14] has therefore expressed himself as very sceptical of the reality of these depolarisation values. The author's experimental results indicate that the finite depolarisations reported by earlier workers are not trustworthy. However, this conclusion is only tentative, and the author hopes, before long, to take up

[13] H. A. Stuart, *loc. cit.*, p. 194.

[14] G. Placzek, *Quanten Mechanik der Materie und Strahlung*, Teil II, Leipzig, 1934, p. 259.

the purification of argon, and a direct experimental test of the anisotropy of this gas, as well as of other rare gases, particularly helium.

Hydrogen sulphide.—H_2S shows an extremely small depolarisation (0·3%) the reality of which however is quite definite. Of the previous workers, Ramanathan estimated the depolarisation as 1% and Parthasarathy as 0·93%. The depolarisations for other hydride molecules such as HCl, HBr, NH_3, etc., as estimated by Parthasarathy are also of the same order of magnitude. In view of the author's low value for H_2S, it would seem that the other values would also be similarly low. These very low values are not difficult to understand, since, as Stuart[15] remarks, "die Hydridmoleküle HCl, H_2O, H_2S und NH_3, die wir als Pseudoedelgase mit mehreren unpolarisierbaren H-Kernen in einer geminsamen Elektronenwolke auffassen können, trotzdem sie elektrisch unsymmetrisch sind, d.h. ein elektrisches Moment besitzen, einen sehr hohen optischen Symmetriegrad haben".

In conclusion, the author wishes to record his grateful indebtedness to Professor Sir C. V. Raman for valuable guidance and suggestions in the course of the present work.

6. *Summary.*

It is pointed out that the existing depolarisation data of gases and vapours are gravely defective, and a redetermination of the values has been made with improved experimental technique. The results obtained are strikingly different from those of previous workers, and afford at the same time a natural explanation of many of the existing anomalies. The genuine depolarisation of methane appears to be only of the order of 0·3% which is in all probability to be attributed to the highly depolarised vibration Raman lines. The depolarisation shows a steady increase as one goes to the higher members of the homologous series, but the values in all cases are much smaller than they were hitherto assumed to be. Cyclopropane shows a very small depolarisation in conformity with the known small depolarisation of cyclohexane, while propylene shows a high value as would be expected from the presence of the double bond in it. Methyl chloride is more anisotropic than ethyl chloride, and the depolarisation factor of the former is much higher than that of methane. Carbon tetrachloride shows an extremely small depolarisation of 0·15% which is discussed in detail. It is tentatively concluded that the depolarisation of argon is nil. The depolarisation of H_2S is only 0·3%. An explanation is offered for the low depolarisation of the hydride molecules in general.

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[15] H. A. Stuart, *loc. cit.*, p. 190.

INFLUENCE OF THE FORMATION OF HYDRATES ON THE DIAMAGNETISM OF CHEMICAL COMPOUNDS.

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1. *Introduction.*

In a previous paper[1] (hereafter referred to as Part I) a study was made of the diamagnetic susceptibilities of liquid mixtures from the point of view of additive law. It is shown that magnetic measurements are not sensitive to interaction effects, whether between like or unlike molecules, carrying high dipole moments. Break-up of association by heating or by the addition of foreign molecules does not produce any change in the value of the mass susceptibility. In this paper, a study has been made of the influence of chemical action on diamagnetism, particularly when hydration is concerned.

Recently Cabrera and Fahlenbrach[2] working with aqueous solutions of potassium iodide observed a small but definite change in the susceptibility value which they attribute to hydration. They suggest that this change is due to the deformation of the ion brought about by hydration. It is with the object of verifying whether such small changes could be observed in magnetic measurements that a study of the decahydrate of sodium sulphate (Na_2SO_4, $10H_2O$), both in solution and in the solid state was undertaken. This salt commends itself as specially suited for this purpose since, as is well known, it decomposes into anhydrous Na_2SO_4 on heating to temperatures above 33°C.

A study of sulphuric acid-water mixtures has also been carried out since several hydrates of the acid are known. The fact that this acid (which is an electrolyte) gives a change in susceptibility on forming a compound gives additional interest to this study. Farquharson[3] has studied this mixture with the Curie-Cheneveau balance. His concentration-susceptibility curve deviates considerably from the additive law and abounds in maxima and minima.

Another mixture which has been studied is acetic acid-water. This is one of great importance since evidence regarding the formation of a compound at equimolecular concentrations is quite definite both from Raman effect data and from viscosity measurements. Besides, Sibaiya and

[1] *Proc. Ind. Acad. Sci.*, 1934, **1**, 77.
[2] *Zeits. f. Phys.*, 1934, **89**, 166.
[3] *Phil. Mag.*, 1931, **12**, 283.

Venkataramiah[4] have studied the magnetic properties of the liquid mixture and showed that the diamagnetic susceptibility decreased considerably (by about 12 per cent.) at equimolecular concentrations. Hence a study of this mixture has been made at different temperatures to test whether the compound formation has any effect on susceptibility. If so, a progressive variation must be noted when an equimolecular mixture is heated. Such deviations have not been observed in the present investigation.

TABLE I.

Sulphuric acid-water.

Sample I		Sample II		Sample III	
Percentage of acid by weight	χ	Percentage of acid by weight	χ	Percentage of acid by weight	χ
0·0	0·720	0·0	0·720	0·0	0·720
7·9	0·686	53·5	0·535	5·1	0·700
21·5	0·628	54·1	0·526	12·3	0·673
40·7	0·565	59·5	0·510	17·8	0·650
46·5	0·541	63·1	0·493	29·8	0·608
49·1	0·540	76·9	0·453	32·5	0·598
53·2	0·529	79·4	0·445	44·5	0·556
65·2	0·482	82·9	0·431	58·8	0·511
71·2	0·469	86·5	0·428	63·1	0·508
82·5	0·432	87·3	0·425	66·0	0·483
97·0	0·403	87·6	0·426	69·4	0·477
		90·5	0·423	69·8	0·474
		93·3	0·416	76·2	0·451
		97·0	0·402	94·5	0·412
				97·4	0·403

2. Experiment.

Two methods of determining the susceptibilities were employed. (*a*) Quincke's method, the details of which are given in Part I and (*b*) Curie method[5] in the special case of sodium sulphate.

[4] *Ind. Jour. Phys.*, 1932, **7**, 393.

[5] Full details of the method are given in *Proc. Ind. Acad. Sci.*, 1934, **1**, 123.

3. *Results.*

(*a*) *Sulphuric acid-water.*—The sulphuric acid used was analytically pure and was taken from freshly opened bottles. Three samples were used. The densities of the pure acid and the mixtures were determined by weighing a clean glass piece suspended by a fine platinum wire, in air, in water and in the liquid. From a knowledge of the density, the concentration of the acid could be found from the tables.

Careful experiments were conducted to test for the presence of iron or other ferromagnetic impurities in the acid. A direct chemical test failed to show the presence of iron. Further the values of the magnetic susceptibility of some mixtures were determined at different field strengths. Results for any given mixture gave a constant value showing the absence of any ferromagnetic impurities.

The mean values obtained for the three samples of sulphuric acid at different concentrations are given in Table I.

Fig. 1 shows the curve between composition and susceptibility. It

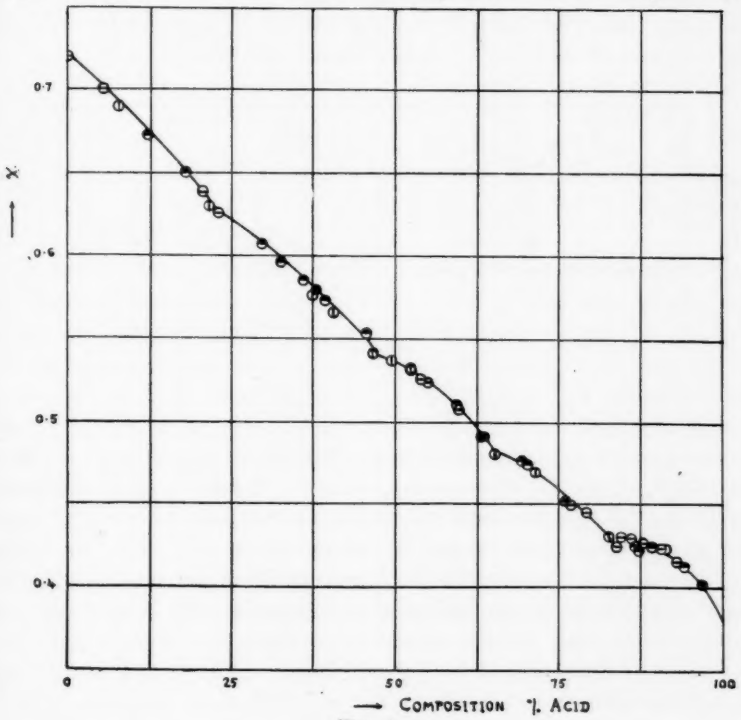

Fig. 1.

is observed that there is considerable departure from the additive law. Singular points in the composition-susceptibility curve may be taken as an indication of an interaction in the system. To find out these singular points better, the deviation from the additive law of mixtures has been plotted against the corresponding concentration. This has been done in Fig. 2. It is seen that the definite formation of hydrates is indicated in the figure, these being $2H_2SO_4$, H_2O ; H_2SO_4, H_2O ; H_2SO_4, $3H_2O$; H_2SO_4, $6H_2O$ and H_2SO_4, $18H_2O$. One point deserves special mention. The susceptibility value corresponding to $2H_2SO_4$, H_2O is greater than the additive value while the values for the other hydrates are smaller than the corresponding additive values. This leads to the definite conclusion that the type of interaction in the case of $2H_2SO_4$, H_2O is different from that of the other hydrates.

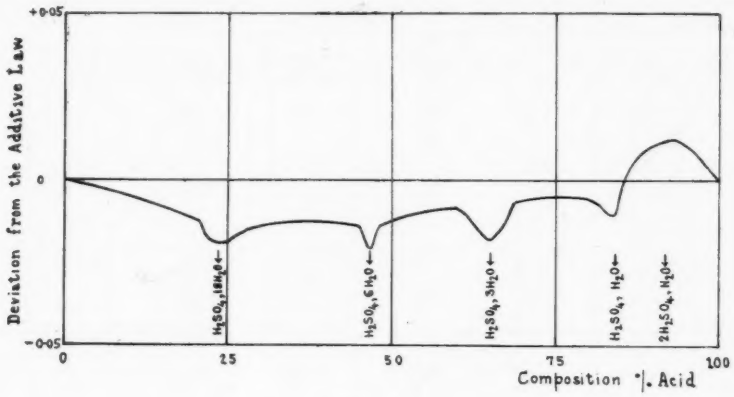

FIG. 2.

It is interesting to compare these results with those of Farquharson. His curve shows a flat maximum at 86–89 per cent. which he suggests as due to H_2SO_4, H_2O. He obtains also a break at the composition corresponding to H_2SO_4, $3H_2O$. Between 0 and 50 per cent. of the acid, he obtains several minor maxima and minima for which he does not offer any explanation. He identifies the decided maximum at 15·1 per cent. as the state in which all the ions are free and obtains a value of $-39{\cdot}0$ for the susceptibility of the SO_4 ion. In the formation of the hydrates H_2SO_4, H_2O and H_2SO_4, $3H_2O$, Farquharson's results and those of the present investigation agree. Our results show clearly by the aid of Fig. 2 that singular points exist at compositions corresponding to a few more hydrates.

Attention may be drawn to the evidence available from other properties regarding the formation of hydrates.[6] The freezing point curves are usually examined to detect the presence of hydrates. It should however be pointed out that while they can be depended upon for solid hydrates separating from solutions, nothing can be inferred regarding the presence of these hydrates in solution. In fact it has been most conclusively shown that even the inert gases can separate out as hydrates on solidification at very low temperatures. This evidence clearly points to the fact that the affinity of the water molecules in the hydrates in the solid state may not be entirely chemical. On the other hand the existence of hydrates in solution points to a more fundamental link of the nature of a chemical bond between the water molecules and the substances under consideration. It is therefore necessary to look in other directions for the identification of the presence of hydrates in solutions.

Deviations from the additive law of mixtures have been plotted against the corresponding concentrations to find singular points by Morgan and Davis. They obtained evidence for the existence of the following hydrates :—H_2SO_4, H_2O by the specific gravity, viscosity and refractive index curves ; H_2SO_4, $2H_2O$ by the refractive index curve, H_2SO_4, $3H_2O$ by the surface tension curve and H_2SO_4, $12\,H_2O$ by the conductivity curve. There is also evidence for the existence of H_2SO_4, H_2O from Graham's investigations on capillary transpiration, and from Thompson's thermochemical observations. Pfaundler and Schnegg discovered the existence of H_2SO_4, H_2O and H_2SO_4, $2H_2O$ from their cryscopic observations.

Bouty found in his electrical conductivity results a minimum for $2H_2SO_4$, H_2O and a maximum for H_2SO_4, H_2O. This is strikingly similar to the susceptibility results obtained in this investigation.

It is seen that hydrates of sulphuric acid having one, two, three, six and twelve molecules of water are all indicated by the different physical properties. The mono-hydrate is indicated by almost all the properties while the hydrate H_2SO_4, $4H_2O$ which crystallises out as a solid, is conspicuous by its absence in solution.

The magnetic observations corroborate the existence of the hydrates, $2H_2SO_4$, H_2O ; H_2SO_4, H_2O ; H_2SO_4, $3H_2O$; H_2SO_4, $6H_2O$ and H_2SO_4, $18H_2O$. The hydrate H_2SO_4, $2H_2O$ seems to be absent in the solution, an observation also made by Farquharson. One of two alternatives is possible. The dihydrate may not be present in the solution under the conditions of the

[6] The information contained in this and the following paragraphs has been taken from Mellor's *Dictionary of Applied Chemistry*, Vol. **10**, p. 353 ff.

experiments or the presence of the dihydrate may not give a break in the susceptibility-concentration curve. This problem needs further investigation.

Sulphuric acid-water mixtures have been studied from the point of view of the Raman Effect by Ramakrishna Rao,[7] Nisi[8] and Woodward.[9] The results show that the Raman frequencies 416, 562 and 1171 are affected considerably by the nature of the combination. The magnetic results outlined above, support the conclusions of Nisi that there are changes of frequency due to the formation of hydrates on dilution of the concentrated acid.

(*b*) *Acetic acid-water.*—Since the density difference between acetic acid and water is small, the method followed in the case of sulphuric acid-water mixtures to determine the composition of any mixture could not be adopted in this instance. Weighed quantities of the acid and water were mixed together and poured into the tube. On exhaustion and sealing, the loss of weight of the mixture by evaporation was only $\frac{1}{2}$ per cent. of the total weight of the mixture. The composition of the liquid inside the tube was taken to be therefore the same as the value before exhaustion, the error in this determination being obviously less than $\frac{1}{2}$ per cent.

TABLE II.

Acetic acid-water.

(Temperature 29° C.)

Acetic Acid %	Depression divisions on scale	χ
0	641·5	0·720
21·4	607·5	0·681
40·7	573·0	0·642
63·1	540·5	0·606
75·0	521·5	0·582
75·4	517·5	0·580
81·8	510·5	0·572
88·3	501·5	0·562
100·0	480·0	0·538

[7] *Ind. Jour. Phys.*, 1933, **8**, 123.
[8] *Jap. Jour. Phys.*, 1929, **5**, 119.
[9] *Phys. Zeits.*, 1931, **32**, 212; *Proc. Roy. Soc.*, 1934, **114**, 118.

The results for the susceptibility of acetic acid-water mixtures at different concentrations are given in Table II.

Table III gives the effect of temperature on the susceptibility of pure acetic acid and water.

TABLE III.

Acetic Acid			Water		
Temperature °C.	χ	χ_t/χ_{30}	Temperature °C.	χ	χ_t/χ_{30}
28	0·538	1·000	28	0·7200	1·0000
29	0·537	0·998	36	0·7202	1·0003
38	0·538	1·000	40	0·7206	1·0008
45	0·538	1·000	45	0·7211	1·0015
53	0·537	0·998	55	0·7216	1·0022
57	0·537	0·998			

The effect of temperature on the susceptibility of the mixtures is shown in Table IV.

TABLE IV.

Acetic Acid 88·3%		Acetic Acid 75%		Acetic Acid 21·4%	
Temperature °C.	χ	Temperature °C.	χ	Temperature °C.	χ
28	0·562	29	0·582	28	0·681
39	0·562	37	0·584	40	0·681
41	0·563	43	0·584	46	0·681
47	0·562	48	0·583	50	0·681
49	0·562	57	0·583		
50	0·562				
56	0·562				

It is seen from Table III that acetic acid shows no variation of susceptibility with temperature in spite of the fact that it has a high dipole moment and is highly associated at ordinary temperatures. The break-up of association in the case of acetic acid as in that of nitrobenzene produces no

change of susceptibility. The results accord well with those of Cabrera and Fahlenbrach.[10] In the case of water, on the other hand, a small definite increase is noted, the coefficient being nearly equal to the values obtained by Auer[11], Cabrera and Fahlenbrach[12] and Boeker[13].

In Fig. 3 is shown a graph between the percentage of acetic acid in the mixture and susceptibility. It is seen that the points plot smoothly on a straight line. No deviations such as were observed by Sibaiya and Venkataramiah are present in the graph.

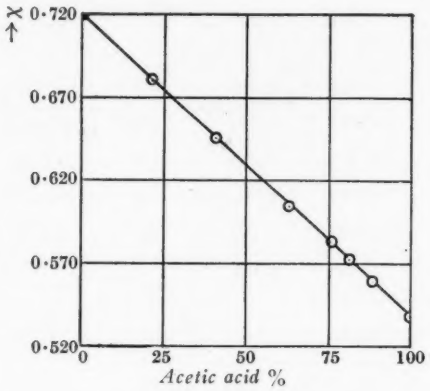

FIG. 3.

This mixture has special interest because of the fact that a definite compound is formed at the particular composition where the coefficient of viscosity is maximum. It is interesting to note that the position of the maximum in the composition-viscosity curve is independent of temperature showing the existence of a definite compound at that concentration.[14] The density curve also shows a maximum at the same concentration. Krishnamurthi[15] has investigated the mixture from the point of view of the Raman effect; his results show that in addition to 1667 cm.$^{-1}$ line characteristic of the acid, a new line at 1707 cm.$^{-1}$ appears at about 95% which increases in intensity with further dilution till it is the only line present at about 75% and lower concentrations of the acid. He further suggests from the intensity variations that the covalent linkage is strengthened in this case. However

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10 *Zeits. f. Phys.*, 1934, **89**, 682.
11 *Ann. der Phys.*, 1933, **18**, 593.
12 *Zeits. f. Phys.*, 1933, **82**, 759.
13 *Phys. Rev.*, 1934, **46**, 907.
14 *Jour. Chem. Soc.*, 1909, **95**, 1556.
15 *Nature*, 1931, **128**, 639.

no deviations from the additive law are caused by the compound formation in magnetic susceptibility measurements.

Increase of temperature produces no change in susceptibility. If any change of susceptibility is brought about by the compound formation, such changes must show alterations with temperature and departures from the additive law ought to occur at higher temperatures. The absence of such an effect proves that no measurable change has been caused by the formation of the compound and any change that takes place is too feeble to affect the electronic system considerably.

(*c*) *Sodium sulphate-water.*—This is a case of a strong electrolyte dissolved in water. It is wellknown that sodium sulphate is present in solution as the decahydrate below 33° C. and that it decomposes at higher temperatures. The reaction can be represented thus :—

$$Na_2SO_4,\ 10H_2O \overset{33°C.}{\rightleftharpoons} Na_2SO_4 + 10H_2O$$

The forward reaction is almost instantaneous while the backward reaction takes some time to proceed, so that it is possible to have the anhydrous sodium sulphate below 33° C. for a short time. The solubility curve brings out this point quite clearly since the solubility of the hydrate is entirely different from that of the anhydrous salt.

These facts have been utilised to study the magnetic behaviour of the hydrated salt both in solution and the solid state. Ray-Chaudhuri[16] has determined the magnetic susceptibility of a number of salts when they are hydrated and anhydrous and finds that in a large number of cases, a marked deviation is observed between the calculated additive value of the hydrate and the observed value. He concludes from the investigation that the deviation from the additive law is more prominent in those cases where the heat of formation is large. The fact that the hydrated and the dehydrated salts were prepared separately for the magnetic investigations makes a quantitative study a little doubtful. An obviously better method would be to prepare the hydrated salt and determine the magnetic susceptibility before and after the dehydration, the water remaining in the combined state in one case and free in the other so that the effect of binding alone will be recorded by the change in the magnetic susceptibility value.

This method is not always easy to realise. But it happens that Na_2SO_4 lends itself easily to such investigation since the hydrated salt decomposes on heating to over 33° C. into the anhydrous salt and water. The object

[16] *Zeits. f. Phys.*, 1932, **77**, 271.

of the present investigation is therefore to study the effect of binding on the susceptibility of the hydrate.

The initial temperature of the solution was usually about 28° C. The depressions obtained in the Quincke method were noted just at this temperature and then at higher temperatures as the liquid was gradually heated. No changes in the depression were observed as the temperature was raised to above 33° C. The solution was then cooled to the laboratory temperature and no change was observed even when the measurements were repeated over a considerable period (3 to 4 hours) during which interval, the salt should have become a hydrate again. This result definitely indicates that no important change in the electronic configuration occurs on dehydration. The values obtained at different temperatures are tabulated below.

TABLE V.

Concentration 11·6%			Concentration 20·0%			Concentration 25·5%		
Temperature °C.	Depression divisions on scale	χ_t/χ_{28}	Temperature °C.	Depression divisions on scale	χ_t/χ_{28}	Temperature °C.	Depression divisions on scale	χ_t/χ_{28}
28	604·0	1·0000	28	581·0	1·0000	28	556·5	1·0000
31	604·1	1·0002	35	580·5	0·9991	31	557·0	1·0009
35	604·5	1·0008	38	581·0	1·0000	36	557·2	1·0012
40	604·3	1·0005	42	581·2	1·0003	40	556·8	1·0005
44	605·0	1·0016	44	581·0	1·0000	42	557·0	1·0009

The measurements have been made at three different concentrations. It is found that the value of the susceptibility remains constant for any concentration when the temperature is raised from 28° C. to 44° C. It is thus clear that whether water exists as water of crystallisation with sodium sulphate or separately, the susceptibility is the same.

The results obtained with the Curie balance also supports the same conclusions. The solid was sealed in a bulb and the deflection was noted. The bulb was then heated gently to temperatures above 33° C. and the deflection taken again. A large number of readings were taken. About 66 to 70 milligrams of the hydrated crystal gave deflections varying from 8 to 9 centimetres. Heating to temperatures above 33° C. did not produce any change in the deflection and hence in the mass susceptibility of the solid when the water of hydration became free and the salt was anhydrous.

4. *Discussion.*

The molecular susceptibility of a polyatomic molecule without a resultant spin is represented according to Van Vleck[17] by the expression

$$\chi_{mol} = -\frac{Le^2}{6mc^2}\Sigma\,\overline{r^2}+\frac{2}{3}L\,\Sigma\,\frac{|\,m_0(n';\,n)\,|^2}{h\nu(n';\,n)}$$

The first term is the well-known term of Langevin while the second is a paramagnetic term independent of temperature and is brought about by the distortion of the electron system due to interatomic forces such as are obtained in diatomic and polyatomic molecules. The substance is diamagnetic or paramagnetic depending on whether the first or the second term is the greater. The second term is however usually small, although the difference between the observed and theoretical values of the susceptibility in the case of some sulphur compounds has been found to be as much as 30 per cent. It is evident from the discussion that the paramagnetic term should vary with the different linkages in the molecule and an additional linkage would mean an increase of this term and hence a decrease in the diamagnetic susceptibility. In solutions, the ions are not free but attach themselves to solvent molecules[18] and thus because of the irregular spacing of a liquid, sufficient asymmetry is brought about resulting in a distortion of the electron system. When a salt is dissolved in a liquid, the binding in the solid state is broken off and at the same time new constraints are brought about because of the attachment of the solvent molecules to the different ions of the salt. The change in susceptibility that ought to be expected therefore when a salt is dissolved in a liquid is due to the difference in the paramagnetic term when in the solid state and in solution. The diamagnetic susceptibility in the solid state would consequently be greater or smaller according as the binding in the solid state is smaller or greater than that in solution. Also if new linkages are formed the system will be affected and the deviation of the susceptibility value will indicate in each case the nature of the linkages involved.

We can also draw attention to the fact that hydration of the ions in solution would indicate greater constraint on the ion and hence the paramagnetic term would become greater resulting in a smaller value for the diamagnetic susceptibility.

In the light of these conclusions, the results for aqueous solutions of sulphuric acid, acetic acid and sodium sulphate are quite interesting. In the case of sulphuric acid-water mixture, we meet with two types of deviations.

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[17] Van Vleck, *Theory of Electric and Magnetic Susceptibility*, p. 275.

[18] Fajans, *Trans. Faraday Soc.*, 1927, **23**, 357.

At 91·6 per cent. of the acid, the hydrate $2H_2SO_4$, H_2O is formed and it gives an increase in the susceptibility value; whereas the other hydrates give lower values. It is easy to understand the decrease of diamagnetic susceptibility in the case of the higher hydrates; but the increase in the case of $2H_2SO_4$, H_2O requires some explanation.

We shall now show that the considerable deformation produced in the SO_4^{--} ion by the hydrogen cations on combination is somewhat reduced by the water molecules and since the paramagnetic term in the above equation is consequently decreased, the diamagnetic susceptibility shows an increase. These assumptions are justified by Raman effect and X-ray data.

Krishnamurthi[19] has studied the effect of the cation on the sulphate group and has come to the conclusion that the smaller cations have greater deforming power. Thus it would appear that H^+ would have a large deforming power on the anion. That there is considerable influence on the Raman frequencies of the anion by the cation and that the smaller cations produce much larger changes are amply borne out by the investigations of Gerlach and Embirikos.[20]

These conclusions receive additional confirmation from the study of the *k* absorption edges. Lindh[21] has shown that the frequency of the continuous *k* absorption edge of an element in a compound radical varies with its valency. In the case of positive ions like those of chromium, manganese and iron, the separation increases with the valency. De Broglie[22] and Lindsay and Voorhes[23] have also verified these conclusions. In the case of anions, the absorption edge shifts towards shorter wave-length as their deformations are increased. Introduction of a neutral molecule like water between the positive and negative ions lowers the deformation of the anions on account of increased distance and hence the absorption edge is shifted towards longer wavelength which indicates that the binding has become more loose.

In the magnetic case, it has been noted that the term Δ in the Curie-Weiss law, which is primarily due to interatomic forces, is almost zero for salts of high magnetic dilution such as $MnSO_4(NH_4)_2SO_4 \cdot 6H_2O$ and $Fe_2(SO_4)_3(NH_4)_2SO_4 \cdot 24H_2O$. In both cases the term Δ is nearly zero since there are large numbers of ammonia and water molecules which lessen the interatomic forces considerably.[24]

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[19] *Ind. Jour. Phys.*, 1930, 513 and 651.
[20] Taken from Kohlrausch, *Smekal-Raman Effect*, p. 204.
[21] *Zeits. f. Phys.*, 1925, **31**, 210.
[22] De Broglie, *X-Rays* (Eng. Trans.), p. 75.
[23] *Phil. Mag.*, 1928, **6**, 910.
[24] *Theory of Electric and Magnetic Susceptibilities*, p. 304.

The case of $2H_2SO_4$, H_2O can be considered as another example where we have a similar dilution effect. The introduction of water molecules loosens the bond between the hydrogen ions and the sulphate ion and hence decreases the deformation. This is accompanied by an increase in the diamagnetic susceptibility. There is considerable evidence, in fact, in favour of the idea of the penetration of the proton into the chloride ion in the case of HCl.[25] Such a penetration would cause a general contraction more especially of the superficial orbits which contribute the largest share to the diamagnetic susceptibility. The loosening of the bond with water would therefore mean an increase in value.

As contradistinguished from this effect, we have the formation of the other hydrates which result in a decrease in diamagnetism. In these cases the water molecules form compounds with the acid and the distortion produced by them is greater than the loosening effect produced when the water molecules are first introduced. A reference to Fig. 2 also indicates that the law of mass action is applicable to the formation of these hydrates.

In the case of acetic acid-water, a compound is formed and the alteration introduced into the electronic system is so small that there is no sensible deviation from the additivity law. The break-up of the decahydrate of sodium sulphate at temperatures higher than 33°C. is not also accompanied by any change of susceptibility at any rate to any measurable extent. The nature of combination in this case is no doubt very loose for it is well known that the sodium sulphate crystals give out their water of crystallisation very easily ; on the other hand, sulphuric acid *absorbs* water vapour very strongly to form stable hydrates.

Attention was drawn to the investigations of Cabrera and Fahlenbrach who studied aqueous solutions of potassium iodide and observed changes in the magnetic susceptibility due to different degrees of hydration. They suggest that there is greater hydration at higher temperatures and that there is an increase of susceptibility corresponding to greater deformation of the ion with increasing hydration. One should expect however a decrease in hydration with increasing temperature. Besides it is quite unlikely that hydration is accompanied by an increase in susceptibility, although in the case of $2H_2SO_4$, H_2O there is an increase for reasons mentioned earlier in the paper. Such an explanation in the case of potassium iodide and generally of strong electrolytes seems to be not justifiable since we have no reason to believe that the distortion caused by hydration itself could be less than the crystalline forces in the solid. It is to be recalled that sulphuric acid

[25] Bell, *Phil. Mag.*, 1924, **47**, 549.

is not as strong an electrolyte as the alkaline halides. The condition for electro-valency tending to become covalent is that the anion must be large and the cation must be very small. This condition being fulfilled in the case of the acid, we ought to expect sulphuric acid to be less electrovalent than the salts mentioned. This indeed is the case as evidenced by the comparatively low dissociation factor of the acid. A break-up of the molecule therefore causes the removal of a large deformation.

Hocart[26] however records a larger susceptibility for a salt in solution than the crystalline state. This difference has been explained by Weiss as being due to deformation in the ion and from the *experimental* values of refractivity a correction has been applied. However there seems to be no real difference between the susceptibility as calculated from the solid state and from the state in solution, provided the depolymerisation of water due to the introduction of the electrolyte is taken into account. In the case of KCl and NaCl for which accurate data are available,[26] it is found that an increase of 0·0018 and 0·003 in the susceptibility of water due to depolymerisation (on the addition of 22% and 25% of KCl and NaCl respectively) would explain the increase observed. When due allowance is made for incidental errors, it looks very probable that this increase is due to depolymerisation of water which has been amply borne out by Raman effect data. It may be mentioned here that measurements in solution must be taken at different increasing temperatures and that the value of the solution which is not altered on increase of temperature, must be used in the calculation of ionic values. In that case the value assumed for water must be that in the completely depolymerised state. Calculations not based on these principles may be in error by as much as 4%.

It thus looks improbable that in these cases hydration causes any change in the susceptibility due to deformation of the ions. The results for sodium sulphate and acetic acid show definitely the comparative insensitivity of diamagnetism to small changes. It may be therefore concluded that the observed changes of Cabrera and Fahlenbrach are to be attributed partly to depolymerisation effects of the ions of water. It is interesting to note that Tammann[27] in a recent communication has drawn attention to the changes in ice VI molecule under the altered conditions of internal pressure brought about by the salt and the increasing temperature. More data on different salts in solution are necessary to decide this important issue. A determination of the susceptibility of water at still higher temperatures

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[26] *Comp. Rend.*, 1929, **188**, 1151.
[27] *Zeits. f. Phys.*, 1934, **91**, 410.

would throw light on the interesting question of the existence of ice VI molecule.

5. *Summary and Conclusions.*

The magnetic susceptibilities of sulphuric acid-water mixtures have been studied at different concentrations. Above 86% of the acid, the susceptibility values are greater than those given by the additive law while below 86%, the values are lower than the additive values. Maximum deviations were observed at concentrations corresponding to $2H_2SO_4$, H_2O; H_2SO_4, H_2O; H_2O_4, $3H_2O$; H_2SO_4, $6H_2O$ and H_2SO_4, $18H_2O$. These hydrates are also indicated by other physical properties of the mixture. The deviations have been accounted for as being due to increased deformation of the anion in the acid in one case and decreased deformation in the other.

Acetic acid-water mixtures have been investigated at different concentrations. The results show that the additive law is obeyed even at equimolecular concentration of the components although a compound is formed at this composition.

The decahydrate of sodium sulphate has been studied both in the solid state by the Curie method and in solution by the modified Quincke method used for sulphuric acid-water mixtures. When the hydrate was heated to more than 33° C. (at which temperature the water of crystallisation breaks away and the crystal becomes anhydrous) no change of magnetic susceptibility was noted. This suggests that the binding of the water molecules to the sulphate is very loose in contradistinction to the case of the hydrates of sulphuric acid. The theoretical basis for the increase of susceptibility on hydration suggested by Cabrera and Fahlenbrach to explain their results in aqueous solutions of potassium iodide is critically examined and evidence is put forward to show that no such changes are likely to occur.

I take this opportunity to express my indebtedness to Dr. S. Ramachandra Rao for his keen interest and helpful guidance. My thanks are due to Mr. S. Narayanaswami Ayyar for much valuable discussion. I thank also the authorities of the Annamalai University for the award of a studentship, which has rendered this work possible.

IRRATIONAL INDEFINITE QUADRATIC FORMS.

By S. Chowla,
Andhra University, Waltair.

Received July 13, 1935.

1. I have recently proved the

Theorem.[1] *If the* c's *are not all of one sign and if all the ratios* $\frac{c_s}{c_t}$ $(s \neq t)$ *are irrational, we can find integers* $n_1, \cdots, n_r$ *(not all zero) such that*

$$\left| \sum_{s=1}^{r} c_s n_s^2 \right| < \epsilon$$

where ϵ *is an arbitrary positive number and* $r \geqslant 9$.

This was deduced from a theorem of Jarnik and Walfisz in the theory of lattice points.

In the same direction we have

Theorem 1. Let $c_1, c_2 > 0$, $\sqrt{\frac{c_1}{c_2}}$ *irrational,*

$$(1) \qquad \sqrt{\frac{c_1}{c_2}} = a_1 + \frac{1}{a_2 +} \; \frac{1}{a_3 + \cdots}$$

Then, to every positive ϵ, *we can find infinitely many pairs of positive integers* n_1 *and* n_2, *such that*

$$(2) \qquad | n_1^2 c_1 - n_2^2 c_2 | < \epsilon$$

whenever $a_n \neq O(1)$, *but not otherwise.*

Theorem 2. If the c's *are not all of one sign, then for* ' *almost all* ' *sets* $(c_1, c_2, \ldots, c_r)$ *we can find integers* $n_1, \ldots, n_r$ *(not all zero) such that*

$$\left| \sum_{s=1}^{r} c_s n_s^2 \right| < \epsilon$$

where ϵ *is an arbitrary positive number and* $r \geqslant 2$.

2. Let $\frac{p_n}{q_n}$ be the nth convergent to (1).

Then

$$(3) \qquad \left| \frac{p_n}{q_n} - \sqrt{\frac{c_1}{c_2}} \right| < \frac{1}{a_n q_n^2}.$$

[1] *Jour. London Math. Soc.*, 1934, **9**, 162-63.

Further, (2) requires,

$$(4) \quad \left| \frac{n_2}{n_1} - \sqrt{\frac{c_1}{c_2}} \right| = 0\left(\frac{1}{n_1^2}\right)$$

From (3) and (4) we obtain Theorem 1, since a_n is unbounded.

To prove Theorem 2, we can assume without loss of generality that c_1 and c_2 have opposite signs. Let $c_1 = b_1 > 0$, $c_2 = -b_2$. Then $b_1 > 0$, $b_2 > 0$.

We know that if

$$\theta = d_1 + \frac{1}{d_2 +} \quad \frac{1}{d_3 + \cdots}$$

where the d's are positive integers, then $d_n \neq O(1)$ for almost all θ. It now follows from Theorem 1 that for almost all (b_1, b_2) we can find positive integers n_1 and n_2 such that

$$(5) \quad | b_1 n_1^2 - b_2 n_2^2 | < \epsilon$$

where ϵ is an arbitrary positive number. Hence for almost all sets (b_1, b_2) we have from (5),

$$(6) \quad | b_1 n_1^2 - b_2 n_2^2 + c_3 . 0^2 + c_4 . 0^2 + \cdots + c_r . 0^2 | < \epsilon \; [n_1, n_2 > 0].$$

Hence Theorem 2 follows from (6), as we can take $n_3 = \cdots = n_r = 0$.

If in Theorem 2 we require that the integers $n_1, \cdots, n_r$ are *all different from zero*, then Theorem 2 is no longer easy to prove -- there is, however, little doubt that the theorem is true even with this restriction.

POSITIVE DETERMINANTS OF BINARY QUADRATIC FORMS WHOSE CLASS-NUMBER IS 2.

By M. Suryanarayana, B.A. (Hons.), B.Ed.

Received July 13, 1935.
(Communicated by Dr. S. Chowla.)

1. Schaffstein[1] has given a list of *positive prime discriminants* of binary quadratic forms whose class-number is 1. His table shows that the majority of *positive discriminants* under 10000 has their class-number equal to 1.

This paper contains a list of *positive prime determinants* [$\equiv 3(4)$] of binary quadratic forms whose class-number is 2. The table extends to positive determinants under 5000, and here again we find that by far the greater majority of determinants considered has the property in question.

2. To test whether $h(d) = 2$ where d is a positive prime $\equiv 3(4)$ and $h(d)$ is the class-number of binary quadratic forms of determinant d, the following test, suggested to me by Dr. S. Chowla, was used (the proof of the 'test' is implicit in known results) :

Let $d \equiv 3(4)$, $d > 0$. *Let* p *denote any prime factor of* $d - x^2$ $(x < \sqrt{d})$, $p < \sqrt{d}$. *Then* $h(d) = 2$ *if* p *occurs as a 'partial quotient' in the simple continued fraction for* $\sqrt{d}$.

(1) The following are values of $d < 2000$ for which $h(d) = 2$, the values of d for which $h(d) > 2$ are marked with an asterisk :

7, 11, 19, 23, 31, 43, 47, 59, 67, 71, 79*, 83, 103, 107, 127, 131, 139, 151, 163, 167, 179, 191, 199, 211, 223*, 227, 239, 251, 263, 271, 283, 307, 311, 331, 347, 359*, 367, 379, 383, 419, 431, 439*, 443*, 463, 467, 479, 487, 491, 499*, 503, 523, 547, 563, 571, 587, 599, 607, 619, 631, 643, 647, 659*, 683, 691, 719, 727*, 739, 743, 751, 787, 811, 823, 827, 839*, 859, 863, 883, 887, 907, 911, 919, 947, 967, 971, 983, 991.

1019, 1031, 1039, 1051, 1063, 1087*, 1091*, 1103, 1123, 1151, 1163, 1171*, 1187, 1223*, 1231, 1259, 1279, 1283, 1291, 1303, 1307, 1319, 1327*, 1367*, 1399, 1423, 1427, 1439, 1447, 1451, 1459, 1471, 1483, 1487, 1499, 1511, 1523*, 1531, 1543, 1559, 1567*, 1571, 1579, 1583, 1607, 1619, 1627*, 1663, 1667, 1699, 1723, 1747, 1759, 1783, 1787*, 1811*, 1823, 1831, 1847*, 1867, 1871, 1879, 1907*, 1931, 1951, 1979, 1987, 1999.

[1] *Math. Annalen*, 1927.

(2) The following are the *only* prime values of $d \equiv 3(4)$ for which $h(d) > 2$, $2000 < d < 5000$:

2027, 2099, 2143, 2207, 2251, 2399, 2459, 2467, 2543, 2659, 2711, 2971, 3023, 3163, 3203, 3251, 3271, 3391, 3719, 3739, 3803, 3967, 4139, 4159, 4271, 4283, 4591, 4651, 4759.

3. Of the 335 primes $d \equiv 3(4)$ upto 5000, 284 primes satisfy $h(d) = 2$, while 51 do not.

I am indebted to Dr. S. Chowla under whose guidance I worked.

ON SUMS OF POWERS.

By Inder Chowla.

Received July 22, 1935.
(Communicated by Dr. S. Chowla.)

1. A non-trivial solution of the equation

$$(1) \quad x_1^k + x_2^k + \cdots + x_m^k = y_1^k + \cdots + y_n^k$$

in positive integers is one in which no x is equal to any y and

$$(x_1, \cdots, x_m, y_1, \cdots, y_n) = 1.$$

When there exists a non-trivial solution of (1) we write

$$(2) \quad (m)^k = (n)^k$$

We use $\beta = \beta(k)$ to denote the least value of n such that (1) has a non-trivial solution with $m < n$, and $\gamma = \gamma(k)$ to denote the least value of n such that (1) has an infinity of non-trivial solutions with $m < n$.

We use $r_{k,s}(N)$ for the number of representations of N as a sum of s positive kth powers (permutation of the bases not being allowed) and $r'_{k,s}(N)$ for the number of primitive representations.

Wright[1] has shown that

Theorem 1. *For* $3 \leqslant k \leqslant 9$ *we have* $\gamma(k) \leqslant k$.

Rao[2] has shown that

Theorem 2. *For* $4 \leqslant k \leqslant 8$ *we have* $\beta(k) \leqslant k-1$.

I prove here that

$$(3) \quad \beta(9) \leqslant 8$$

so that we obtain

Theorem 3. *For* $3 \leqslant k \leqslant 9$ *we have* $\beta(k) \leqslant k - 1$.

I also find that

Theorem 4.

(i) $(5)^7 = (5)^7$

(ii) $(4)^7 = (6)^7$

(iii) $(7)^9 = (7)^9$

Of these relations (ii) and (iii) are new, while (i) has also been established by Rao in a paper to appear in *Mathematische Zeitschrift*.

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[1] *Journ. London Math. Soc.*, 1935, **10**.

[2] The cases $k=5$, 6, 8 in *Journ. London Math. Soc.*, 1934, **9**, 170-71, 172-73 and *Mathematische Zeitschrift*, 1934, **39**, 240-43. The case $k=7$ in a paper to appear in *Mathematische Zeitschrift*.

Further, Wright[3] has shown that

Theorem 5. *For* $3 \leqslant k \leqslant 9$,

$$r'_{k,k}(N) \geqslant 2 \text{ is true for infinitely many } N.$$

From Theorem 4, (i) and (iii) we deduce that

Theorem 6. *For* $k = 7$ *and for* $k = 9$,

$$r'_{k,k-1}(N) \geqslant 2 \text{ is true for infinitely many } N.$$

2. Our Theorem 2 is a special case of

Theorem 7. *For* $r = 1, 3, 5, 7, 9$ *we have*

$$1^r + 4^r + 7^r + 32^r + 33^r + 44^r + 47^r + 48^r = 14^r + 26^r + 39^r + 42^r + 46^r + 49^r$$

In particular, we have,

$$(6)^9 = (8)^9$$

so that $\beta(9) \leqslant 8$.

The results of Theorem 4 are special cases of the following:

(4) $1^r + 5^r + 13^r + 39^r + 51^r + 59^r = 23^r + 33^r + 55^r + 57^r \quad [r = 1, 3, 5, 7]$.

(5) $7^r + 11^r + 19^r + 61^r + 69^r + 91^r + 93^r = 1^r + 13^r + 25^r + 55^r + 75^r + 87^r + 95^r \; [r = 1, 3, 5, 7, 9]$.

(6) $15^r + 27^r + 51^r + 61^r + 69^r = 13^r + 31^r + 47^r + 65^r + 67^r \quad [r = 1, 3, 5, 7]$.

3. All our results are obtained by "Tarry's process". A complete derivation of the results will appear elsewhere. Our method also proves

Theorem 8. *We have* $\beta(17) \leqslant 31$.

[3] *Loc. cit.*

A PRACTICAL FINANCIAL TRANSACTION.

By G. S. Diwan
and
V. V. Narlikar.

Received July 22, 1935.

A Messenger prize of the Institute of Actuaries, London, was awarded in 1933, for the first time, to an Indian, Mr. D. P. Misra,[1] for demonstrating that multiplicity of the rate of interest is possible for a financial transaction and for propounding the need of a criterion by which a unique rate of interest may be determined in such cases of ambiguity. It had been taken for granted before, presumably without any mathematical proof to support it, that a financial transaction admits only one rate of interest; and hence the examples given by Misra in which two or more rates of interest become possible evoked much interest among the leading actuaries of the world.

A precise definition of a practical financial transaction must first be stated as it is intended to treat it here mathematically. The definition proposed by us is this: throughout a practical financial transaction, on the basis of a uniform rate of interest, the original creditor always remains the creditor, and the original debtor always the debtor and that the two are quits only when the transaction comes to an end. This definition is not satisfied by the examples of Misra wherein multiplicity arises.

The definition of a practical financial transaction may now be expressed as a set of mathematical conditions. Let a financial transaction start with A lending a sum a_0 to B on a certain date, say, January 1st, 1935. If A is the creditor $a_0 > 0$. Exactly a year from that date A lends another sum a_1 to B or B returns a sum $-a_1$ to A according as a_1 is +ve or −ve. If $y\%$ is the rate of interest we may denote $1+y/100$ by x. According to the definition of a practical transaction $a_0x + a_1 \geqslant 0$ on January 1st, 1936. If $a_0x + a_1 = 0$ the transaction becomes complete and the rate of interest is $10^2\,(-a_1/a_0 - 1)\%$. If the transaction is not complete on January 1st, 1936, let it be completed exactly n years after the initial payment. If at the end of the rth year from the beginning A lends a_r to B or B returns $-a_r$ to A according as a_r is +ve or −ve, then the following algebraic conditions hold good:

[1] *Journal of the Institute of Actuaries*, Vol. 64, pp. 71-97. *Vide* also Dr. Steffensen's paper in the same volume.

$$\left.\begin{aligned} f_n(x) &\equiv a_0x^n + a_1x^{n-1} + \cdots + a_n = 0 \\ f_r(x) &\equiv a_0x^r + a_1x^{r-1} + \cdots + a_r > 0,\ r = 0, 1, \cdots, n-1 \end{aligned}\right\} \quad .. \quad \text{(I)}$$

If $a_r = 0$ it means of course that no payment occurs between the parties at the end of the rth year. The uniqueness will be established when we prove that if there exists a root of $f_n(x) = 0$, say, $x = \alpha > 1$ satisfying all the conditions (I) then there cannot exist $\beta > 1$ satisfying $f_n(x) = 0$. This is an algebraic problem and we proceed to prove now a slightly more general problem :

If $\alpha \geqslant 0$ satisfies all the conditions (I) then $f_n(x) = 0$ has no other positive root.

We have

$$f'_n(x) = [f_{n-1} + x f_{n-2} + \cdots + x^r f_{n-r-1} + \cdots + x^{n-1}f_0] \quad .. \quad .. \quad \text{(II)}$$

It is clear from (II) that at $x = \alpha$ $f'_n(\alpha)$ is positive. As in (II) $f'_{n-1}(x)$, $f'_{n-2}(x)$, etc., may also be expressed by similar finite series. Hence $f'_{n-1}(\alpha)$, $f'_{n-2}(\alpha)$, etc., are all positive. It follows therefore that $f''_n(x)$ is + ve at $x = \alpha$. Proceeding in this manner it becomes clear that $f'''_n(\alpha)$, $f^{IV}_n(\alpha)$, $\cdots$ $f^n_n(\alpha)$ are all positive and that the higher derivatives vanish. Using the Taylor polynomial expansion we find that $f_n(x) > 0$ for $x > \alpha$ and that $f_n(x) = 0$ cannot therefore have another root greater than α.

We can also show that there cannot exist another root β of $f_n(x) = 0$ such that $0 < \beta < \alpha$. For obviously $f_0(\beta) = f_0(\alpha) > 0$. Hence $\alpha f_0(\alpha) + a_1 > \beta f_0(\beta) + a_1$ or $f_1(\alpha) > f_1(\beta)$. Since $f_1(\alpha) > 0$ we obtain similarly $f_2(\alpha) > f_2(\beta)$. Applying this process continuously the conclusion is reached that $f_n(\alpha) > f_n(\beta)$. But $f_n(\alpha) = 0$. Hence β cannot be a root of $f_n(x) = 0$.

It is this algebraic proposition that supplies a proof of the uniqueness of the rate of interest in a practical financial transaction. We have considered the simple case where payments and returns are made at yearly intervals, but a more sophisticated case where payments and returns are made at any intervals which however can be expressed by commensurable integers reduces to a similar algebraic problem to which the result of the general proposition established becomes applicable.

Incidentally the general algebraic proposition is also valid if some, but not all, $f_r(x)$ vanish at $x = \alpha$. The case is certainly trivial where all $f_r(x)$ vanish at $x = \alpha$. It is also evident that the root α is not repeated except possibly when $\alpha = 0$.

When this investigation was being carried out a new theorem in the theory of equations occurred to us. In view of the close connection between the mathematical arguments of this paper and this theorem it may not be

out of place to state and prove it here briefly. Following the notation of the paper we state the theorem as follows :

If $f_r(x) = 0$ has p roots each greater than a, then there are at least p changes of sign in the series $f_0(a), f_1(a), \cdots, f_r(a)$ where $a \geqslant 0$.

Consider $(x-\beta) f_r(x) = \psi_{r+1}(x)$ for $\beta > a$. If $\psi_{r+1}(x) \equiv b_0 x^{r+1} + b_1 x^r + \cdots + b_{r+1}$ we may define $\psi_t(x) \equiv b_0 x^t + b_1 x^{t-1} + \cdots b_t$ for $t = 0, 1, \cdots r$; so that $\psi_t(a) = (a - \beta) f_{t-1}(a) + a_t$, $\psi_0(a) = f_0(a)$ and $\psi_{r+1}(a) = (a-\beta) f_r(a)$. Now consider the signs in the two series :

$$f_0(a) \quad f_1(a) \cdots \cdots f_r(a)$$
$$\psi_0(a) \quad \psi_1(a) \cdots \cdots \psi_{r+1}(a).$$

The two series begin with the same sign and end with opposite signs. Corresponding to a change of sign from $f_{t-1}(a)$ to $f_t(a)$ the sign of $\psi_t(a)$ agrees with the latter ; and corresponding to a continuation of sign in the first from $f_{t-1}(a)$ to $f_t(a)$ the sign of $\psi_t(a)$ remains ambiguous. When a zero value comes in either series we may take the left hand sign.

Hence it follows that the ψ-series has at least one more change of sign than the f-series. If the f-series is perfectly general so also is the ψ series, the increase in changes of sign in the latter series being due to the fact that $\psi_{r+1}(x) = 0$ has one more root (*viz.*, β) exceeding a than $f_r(x) = 0$. This completes the proof of the theorem, which may be regarded as a generalisation of Descartes' rule of signs.

Summary.

A definition of a practical financial transaction is given and it is proved straight from the definition that a practical transaction admits only one rate of interest. The transactions considered by Misra in his paper are thus shown to be only mathematically possible. Two new algebraic theorems are stated and proved.

CHEMISTRY OF β-ARYL GLUTACONIC ACIDS.

Part II. Condensations with Phenolic Ethers.

By G. R. Gogte, M.Sc.

(*From the Department of Organic Chemistry, Indian Institute of Science, Bangalore.*)

Received July 24, 1935.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

Introduction.

In Part I of this series,[1] the β-(β-methoxy-naphthyl)-glutaconic acid was found to be the first case of a glutaconic acid of the β-aryl type to be separated in geometrically isomeric forms, and later on[2] it was found possible to transform all the naphthol substituted glutaconic acids into their geometrical isomerides. In a search for more glutaconic acids belonging to the β-aryl type exhibiting geometrical isomerism, the author happened to condense *p*-cresol-ethylether with acetone-dicarboxylic acid. This condensation, however, gave only one form of a β-(2-ethoxy-5-methyl-phenyl)-glutaconic acid (I), besides two other new acids melting at 205°C. and 232°C. These acids were found to belong to an entirely new type of compounds which could be derived from glutaconic acids, and form the subject of the present investigation.

The equivalents and empirical formulæ of these acids were of a grade differing from the glutaconic acid by about one molecule of *p*-cresol-ethylether, and this combined with their monobasic character, suggested their probable formation by interaction of the cresolether with one of the carboxylic groups of the glutaconic acid during the reaction. However, when it was attempted to condense the glutaconic acid (I) with *p*-cresol-ethylether in the presence of concentrated sulphuric acid as in the original reaction, no reaction was observed to proceed in the expected manner. Similar condensation products of phthalic and succinic acids with aromatic hydrocarbons or phenolic ethers have been obtained in the past from their anhydrides, by the application of Friedel and Crafts' reaction.[3] This reaction

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[1] Gogte, *Proc. Indian Acad. Sci.*, A, 1934, **1**, 48–60.

[2] Gogte, *Proc. Indian Sci. Congress*, 1935, Abst. No. 115.

[3] Pechmann, *Ber.*, 1880, **13**, 1612; Burker, *A.ch.* (5) **26**, 435, 499; Nourrison, *Ber.*, **19**, 2103; Ullmann and Schmidt, *Ber.*, **52**, 2098; Bentley, Gardner and Weizmann, *J.C.S.*, **1907**, 1626.

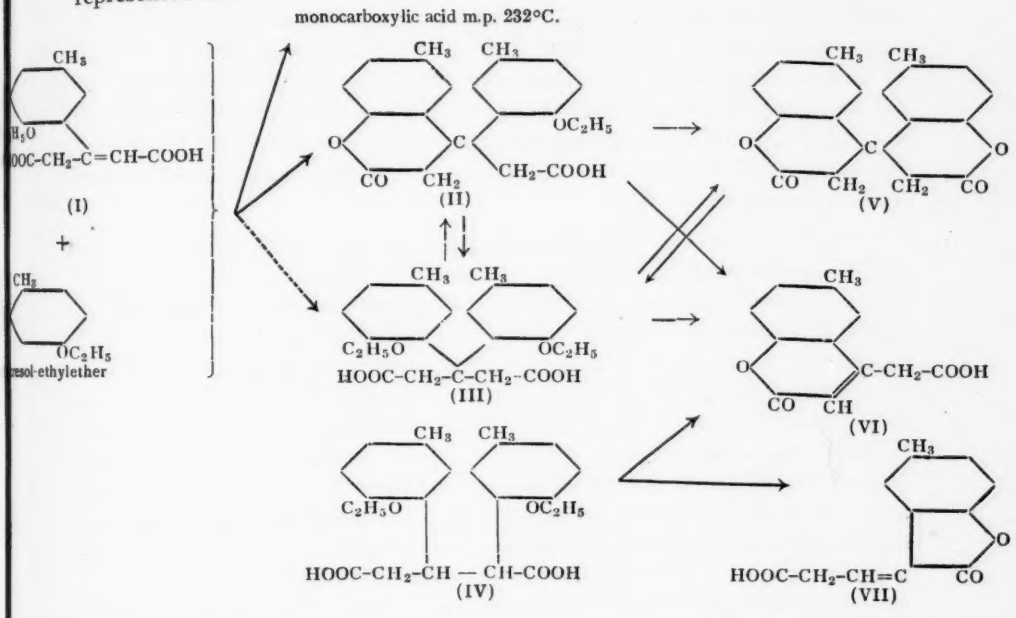
was found unworkable in the present case, in that, the glutaconic anhydride, being an unsaturated compound, was itself attacked by aluminium chloride. Moreover, zinc chloride or phosphorus pentoxide could not be used here as condensing agents, for they transformed the glutaconic acid into its anhydride, which prevented further reaction. The desired condensation, however, was found to get effected, in the presence of 80% sulphuric acid, appreciable quantities of the acids m.p. 205°C. and 232°C. being formed.

The monocarboxylic acid m.p. 205°C., however, did not absorb any bromine from bromine water, did not decolourise alkaline potassium permanganate solution and gave no semicarbazone, thus indicating an absence of any double bond or a ketonic group in itself. This went against the above supposition about its formation. When treated with 80% sulphuric acid this monocarboxylic acid gave the known 6-methyl-coumarin-4-acetic acid[4] (VI), while the action of concentrated sulphuric acid produced together with this coumarin acid, a neutral compound m.p. 184°C. with an empirical formula showing a loss of one molecule of ethyl alcohol during its formation. This neutral compound, on boiling with caustic alkalies, went slowly in solution, and on subsequent acidification produced an acid, which decomposed at 110°C. and gave back the neutral compound. This new acid was also extremely unstable giving back the original neutral compound even on simple crystallisation ; this suggested an existence of a lactone ring similar to that in the coumarins, in the latter. Hydrolysis and subsequent ethylation of the neutral compound to prevent this lactone-ring closure, yielded, instead of the original monocarboxylic acid m.p. 205°C., a new dicarboxylic acid m.p. 219°C. with an empirical formula showing an excess of one molecule of ethyl alcohol over the monocarboxylic acid. This indicated the presence of a lactone ring also in the monocarboxylic acid m.p. 205°C. which was proved by its transformation into the dicarboxylic acid m.p. 219°C. by hydrolysis and ethylation. On the other hand, the dicarboxylic acid m.p. 219°C. was also found to give, by the action of sulphuric acid, a mixture of the monocarboxylic acid m.p. 205°C., the neutral compound m.p. 184°C. and the 6-methyl-coumarin-4-acetic acid (VI).

It was therefore concluded that the dicarboxylic acid m.p. 219°C. was the primary product of the reaction formed evidently by the addition of one molecule of *p*-cresol-ethylether to the *β*-(2-ethoxy-5-methyl-phenyl)-glutaconic acid (I) ; the monocarboxylic acid m.p. 205°C. (II) and the neutral compound m.p. 184°C. (V) being its mono and dilactones. Such direct additions of aromatic hydrocarbons or phenolic ethers to a double bond,

[4] Dey, *J.C.S.*, 1915, 1636.

are known to happen in the case of styrols,[5] and cinnamic acid.[6] Thus here the dicarboxylic acid m.p. 219° C. can be represented by either of the structures (III) and (IV), according to which carbon atom along the double bond, the nucleus of the phenolic ether is attached. The symmetrical structure (III) designating the dicarboxylic acid as ββ′-(22′-diethoxy-55′-dimethyl-diphenyl)-glutaric acid, is the more probable one, because an acid of the structure (IV) would give in addition to the 6-methyl-coumarin-4-acetic acid (VI), an acid of the formulæ (VII) by the action of sulphuric acid ; no such acid was detected. These reactions and all the products could be represented as :



β-Substituted glutaric esters are known to condense with oxalic ester, but the reaction is more difficult when there are two methyl groups in the β-position.[7] The esters of the present glutaric acid could not be made to condense with oxalic ester. This may be due to the fact that there are two much heavier phenolic ether groups in the β-position, which cause a kind of steric hindrance as in the case of ββ-dimethyl-glutaric esters.

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[5] König, *Ber.*, **23**, 3145; Krämer and Spilker, *Ber.*, **23**, 3169, 3269.

[6] Libermann and Hartmann, *Ber.*, **24**, 2582; **25**, 957.

[7] Dieckemann, *Ber.*, 1930, **32**; Komppa, *Annalen*, **368**, 126.

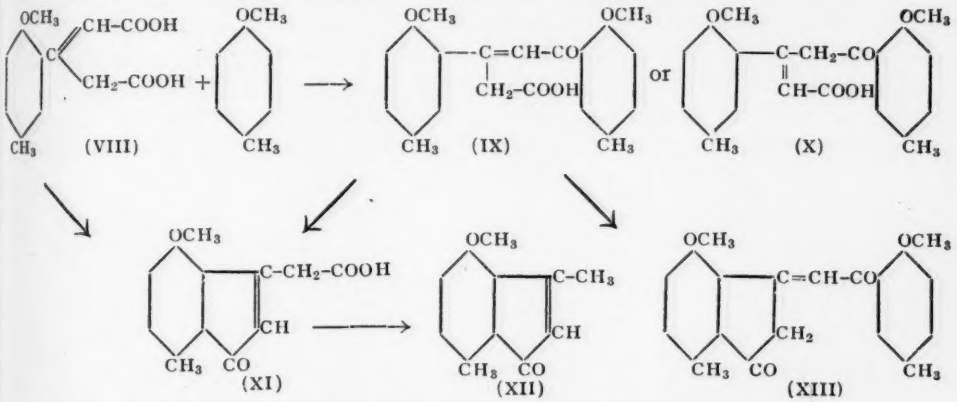
In the other monocarboxylic acid m.p. 232° C., the absorption of bromine from bromine water, the instantaneous decolourisation of alkaline potassium permanganate solution, and the easy formation of semicarbazone indicated the existence of unsaturation and a ketone group. This showed that it had been formed by the elimination of a molecule of water between one of the carboxylic groups of the glutaconic acid (I) and the nuclear hydrogen atom of *p*-cresol-ethylether. A similar monocarboxylic acid melting at 252° C. had been obtained previously by the condensation of *p*-cresol-methylether with acetone-dicarboxylic acid.[8] It has now been found possible to synthesise this also by the condensation of *p*-cresol-methylether with β-(2-methoxy-5-methyl-phenyl)-glutaconic acid (VIII) in the presence of 80% sulphuric acid. It was observed that no glutaric acid like (III) was formed in either of these condensations; the compound could however be synthesised from the dilactone (V) by hydrolysis and methylation. This monocarboxylic acid m.p. 252° C. could be designated by either the structure (IX) or (X), depending upon which of the carboxylic groups of the glutaconic acid had taken part in the reaction.

By the action of 80% sulphuric acid, the monocarboxylic acid m.p. 252° C. produced an indone-acetic acid m.p. 218° C. by the loss of one molecule of *p*-cresol-methylether, which was identical with the one described by Gogte and Limaye[8]; but the action of concentrated sulphuric acid yielded, in addition to the indone-acetic acid, a neutral compound m.p. 214° C. by a loss of water caused by the internal condensation of the carboxylic group with the ring. If the structure (IX) be assumed for the monocarboxylic acid, the indone-acetic acid will have the formula (XI) and the neutral compound (XIII). Then the decarboxylation product (XII) of the indone-acetic acid will not contain a reactive–CH_2–CO–group in the ring, but such a group will be present in the neutral compound. If, on the other hand, the structure (X) represents the monocarboxylic acid, the situation will be exactly reversed and thus a decision between these two alternative formulæ (IX) and (X) can easily be made by examining whether the decarboxylation product of the indone-acetic acid or the neutral compound m.p. 214° C. contains a reactive methylene group by condensing with aromatic aldehydes.[9] It was observed that the neutral compound m.p. 214° C. (XIII) easily condensed with benzaldehyde whereas the decarboxylation product (XII) remained inert, thus supporting the formula (IX) for the monocarboxylic acid m.p. 252° C. This structure is further supported by the observation that

[8] Gogte and Limaye, *J. Univ. Bom.*, **3**, Part II, 135.

[9] Compare Kipping, *J.C.S.*, 1894, **65**, 492.

the esters of the monocarboxylic acid also contained no reactive–CH_2–CO– group condensing with benzaldehyde, as would be the case if formula (X) were correct. In the formula (IX), the carboxylic group of the glutaconic acid is represented as attached at the ortho-position to the methoxy group of the *p*-cresol-methylether, as this is the only reactive position in the nucleus. The monocarboxylic acid m.p. 252° C. can therefore be designated as 2-2′-dimethoxy-5-5′-dimethyl-chalkone-α-acetic acid, and the indone-acetic acid as 7-methoxy-4-methyl-3-keto-indene-acetic acid. The fact that in the formation of these acids, the carboxylic group of the glutaconic acid (VIII) situated at the end of a conjugated system of double bonds, has taken part in the reactions, is in harmony with its increased reactivity. These reactions and the above-mentioned products are represented as :



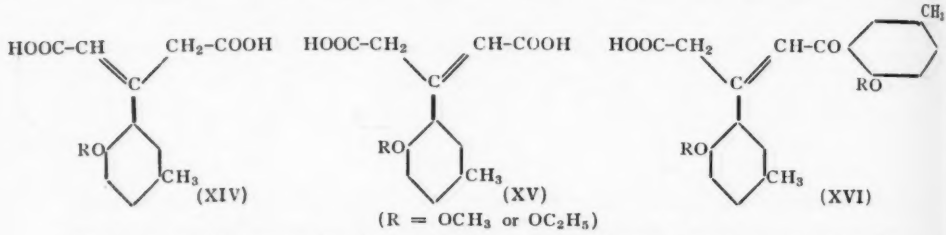
The corresponding monocarboxylic acid m.p. 232° C. obtained in the condensation of *p*-cresol-ethylether, gave by the action of sulphuric acid, an indone-acetic acid m.p. 216° C. and a neutral compound m.p. 165° C. This indone-acetic acid could not however be obtained from the β-(2-ethoxy-5-methyl-phenyl)-glutaconic acid (I) by the action of sulphuric acid, the 6-methyl-coumarin-4-acetic acid being the sole product in this case.

Conclusion.

Pechmann's condensation consists primarily in the elimination of a molecule of water between the enolic hydroxylic group of the β-ketonic ester and the nuclear hydrogen atom of the phenol, whereas in the Simonis' reaction, it is the carboxylic group of the β-ketonic ester that eliminates water with the latter. In the present condensations of *p*-cresol-methyl and ethyl-ethers with acetone-dicarboxylic acid, both these reactions apparently happen simultaneously to produce the chalkone-acetic acids, and thus they

can be looked upon as a combination of Pechmann's and Simonis' reactions. Similarly the glutaric acid condensation can be called a combination of Pechmann's and Krämer's reaction.

The β-(2-methoxy-5-methyl-phenyl)-glutaconic acid (VIII) by the action of sulphuric acid, produces the indone-acetic acid (XI) as well as the 6-methyl-coumarin-4-acetic acid (VI), whereas the β-(2-ethoxy-5-methyl-phenyl)-glutaconic acid (I) gives only the latter coumarin acid, no trace of any indone-acid being obtained. The chalkone-acetic acids m.p. 252° C. and 232° C. (IX) on the other hand, give only the indone-acids (XI) under these circumstances, and not even a trace of the coumarin acid. It thus appears that in the β-(2-ethoxy-5-methyl-phenyl)-glutaconic acid (I) and in both the chalkone-acetic acids, there is a restricted rotation round the bond joining the β-carbon atom of the glutaconic acid to the phenolic ether (shown in thick line). Consequently the β-(2-ethoxy-5-methyl-phenyl)-glutaconic acid can be represented only by the formula (XIV) and the chalkone-acetic acid by (XVI). Thus it must be presumed that in the condensation of this glutaconic acid with *p*-cresol-ethylether, the formation of the chalkone-acetic acid has been preceded by the change of the glutaconic acid from the structure (XIV) to (XV) which alone is capable of producing the indone-acid.



This great difference in the resulting condensation products, caused by the mere replacement of the methoxy group in the *p*-cresol-methyl-ether by ethoxy group, is striking.

Experimental.

Condensation of p-*cresol-ethylether with acetone-dicarboxylic acid.*—Citric acid (200 g.) was finely powdered and covered with concentrated sulphuric acid (240 c.c.). The mixture was shaken well and fuming sulphuric acid (20 per cent. SO_3; 80 c.c.) was gradually added. Immediately a vigorous reaction commenced with frothing and evolution of carbon monoxide, which was completed by heating on a water-bath at 60°C. with shaking at intervals, till a clear orange solution was obtained. It was cooled in a freezing mixture to a temperature of about 2–3° C. and *p*-cresol-ethylether (65 c.c.) was gradually added with shaking. After keeping at this temperature

for 3½ hours, the reaction mixture was poured on 1000 g. of cracked ice, when the sticky mass thus separated turned into a brittle cake on keeping overnight. This was filtered, dissolved in dilute sodium carbonate solution, this solution washed with ether to remove any unchanged *p*-cresol-ethyl-ether and other neutral impurities and acidified. The semisolid mixture of acids thus obtained became granular on rubbing and keeping overnight with water. Yield 47 g.

β-(2-ethoxy-5-methyl-phenyl)-glutaconic acid.—The above mixture of acids was treated with 4 litres of boiling water and filtered, when the filtrates on cooling deposited crystals of the glutaconic acid. It was recrystallised from water as colourless short rods m.p. 153° C. (decomp.). On treating with concentrated sulphuric acid at 60° C., or 80% sulphuric acid overnight, it gave only the 6-methyl-coumarin-4-acetic acid m.p. 180° C. (decomp.) (Found : Eq = 132 ; C = 63·44% ; H = 6·6% ; $C_{14}H_{16}O_5$ requires Eq = 132 ; C = 63·6% ; H = 6·66%).

The *hydroxy-anhydride* crystallised in colourless needles from benzene, m.p. 112° C. It titrates as a monobasic acid and gives phenolic colouration with ferric chloride in cold alcoholic solution (Found : Eq = 243 ; C = 68·15% ; H = 5·6% ; $C_{14}H_{14}O_4$ requires Eq = 246 ; C = 68·29% ; H = 5·69%).

The *semianilide*, prepared from the hydroxy anhydride and aniline in benzene solution, crystallised from 60% aqueous methyl alcohol in hexagonal plates m.p. 136° C. It decomposed after 150° C. temperature to give the anil described below (Found : C = 70·5% ; H = 6·1% ; $C_{20}H_{21}O_4N$ requires C = 70·8% ; H = 6·16%).

The *hydroxy-anil* crystallised from 80% alcohol in yellowish silky needles m.p. 163° C. (Found : C = 74·5% ; H = 5·80% ; $C_{20}H_{19}O_3N$ requires C = 74·76% ; H = 5·90%).

The monolactone of ββ′-(22′-diethoxy-55′-dimethyl-diphenyl)-glutaric acid.—The water insoluble residue in the above (about 15 g.), on crystallisation from alcohol, melted between 190–200° C. This was esterified by alcohol and sulphuric acid and the resulting mixed esters were, by fractional crystallisation from 80% methyl alcohol, separated into two fractions, the more insoluble one melting at 124°C., and the other at 110–115° C. Hydrolysis of the former gave the monolactonic acid which crystallised from alcohol in stout colourless needles, m.p. 205° C. yield 8 g. The acid titrated as monobasic acid and gave an insoluble barium salt in the cold. The acid was soluble in alcohol, acetic acid, acetone, and insoluble in water, benzene, petrol or chloroform (Found : Eq = 356 ; C = 71·00% ; H = 6·12% ; $C_{21}H_{22}O_5$ requires Eq = 354 ; C = 71·2% ; H = 6·2%).

The *ethyl-ester* crystallised from methyl alcohol in colourless hexagonal rods m.p. 124° C. (Found : C=72·1% ; H=6·72% ; $C_{23}H_{26}O_5$ requires C=72·25% ; H=6·8%).

The 22'-diethoxy-55'-dimethyl-chalkone-α-acetic acid.—The more soluble fraction of the mixed ethyl esters melting between 110–115° C., was hydrolysed by alcoholic potash, and the resulting mixture of acids melting between 195–215° C., was dissolved in hot 15% sodium hydroxide solution. On cooling the solution gradually, colourless shining leaflets of a sodium salt separated, which were collected at the pump under strong suction, washed with small amounts of 10% sodium carbonate solution, and acidified in cold by hydrochloric acid. The acid coming out as a fine precipitate was filtered and crystallised from a large amount of alcohol in colourless rectangular plates m.p. 232° C. yield 2 g. The acid is soluble in acetone, sparingly so in alcohol and acetic acid, and insoluble in other organic solvents. It gave an insoluble barium salt in the cold. Its solution in alkali instantaneously decolourised potassium permanganate solution. Its esters did not condense with aromatic aldehydes (Found : C=72·00% ; H=6·7% ; Ba=14·70% ; $C_{23}H_{26}O_5$ requires C=72·25% ; H=6·8% ; $(C_{23}H_{25}O_5)_2Ba$ requires Ba=15·25%).

The *ethyl-ester* prepared by alcohol and sulphuric acid, crystallised from 80% methyl alcohol in colourless parallelogramic plates, m.p. 133° C. (Found : C=72·9% ; H=7·24% ; $C_{25}H_{30}O_5$ requires C=73·2% ; H=7·32%).

Semicarbazone was prepared by refluxing the acid with semicarbazide hydrochloride and sodium acetate in alcoholic solution for 3 hours. On cooling, the semicarbazone separated and when recrystallised from alcohol melted at 264° C. (decomp.) (Found : C=65·3% ; H=6·4% ; $C_{24}H_{29}O_5N_3$ requires C=65·6% ; H=6·6%).

Semicarbazone of the ethyl ester was obtained by refluxing the reactants in alcoholic solution for 7 hours. It crystallised from alcohol in needles m.p. 171° C. (decomp.) (Found : C=66·6% ; H=6·85% ; $C_{26}H_{33}O_5N_3$ requires C=66·8% ; H=7·06%).

Condensation of β-(2-ethoxy-5-methyl-phenyl)-glutaconic acid with p-*cresol-ethylether.*—The recrystallised glutaconic acid (10 g.) was finely powdered and dissolved in previously ice-cooled 80% dilute sulphuric acid—1 vol. water : 4 vol. sulphuric acid—(50 c.c.). The *p*-cresol-ethylether (20 c.c.) was then added gradually with shaking at intervals. On continuing the shaking until the two layers disappeared—about 2 hours—the clear orange solution was allowed to stand at the room temperature for 20 hours. This reaction mixture was then poured on 200 g. of crushed ice, when a sticky

mass separated which became granular on keeping overnight. It was filtered, taken up in dilute sodium carbonate, the solution filtered, washed with ether to remove the excess of *p*-cresol-ethylether, and acidified by hydrochloric acid. The mixed acids were filtered and treated with 400 c.c. of boiling 10% aqueous acetic acid, then with 100 c.c. of boiling water, filtered, and dried. Yield of mixed acids 3·5 g. This was esterified by alcohol and sulphuric acid, and separated into the monolactonic acid m.p. 205° C. yield 2 g., and the chalkone-acetic acid m.p. 232° C. yield 1 g.; exactly as above. The acetic acid filtrate on cooling gave the 6-methyl-coumarin-4-acetic acid.

Action of 80% *sulphuric acid on 22'-diethoxy-55'-dimethyl-diphenyl-chalkone-α-acetic acid: Formation of 7-ethoxy-4-methyl-3-keto-indone-acetic acid.*—The chalkone-acetic acid (2·5 g.) was finely powdered and dissolved in 80% sulphuric acid by rubbing and warming a little. The red fluorescent solution on keeping over-night at the room temperature was poured in water, the precipitate taken up in dilute sodium carbonate, filtered and acidified. The acid was crystallised from alcohol in short yellow needles m.p. 216° C. (decomp.); yield 1 g. The acid is sparingly soluble in alcohol and acetic acid and insoluble in water, benzene, petrol or chloroform. It titrates as a monobasic acid and gives intensely coloured solutions with caustic alkalies. This indone acid could not be obtained from the β-(2-ethoxy-5-methyl-phenyl)-glutaconic acid (Found: C=68·21%; H=5·65%; $C_{14}H_{14}O_4$ requires C=68·3%; H=5·7%).

The *ethyl-ester* prepared from the acid by alcohol and sulphuric acid crystallised from 80% alcohol as yellow flat needles m.p. 169° C. (Found: C=69·8%; H=6·45%; $C_{16}H_{18}O_4$ requires C=70·0%; H=6·57%).

The *semicarbazone* was obtained by refluxing the reactants in alcoholic solution for 2 hours. Light needles m.p. 247° C. (decomp.) (Found: C=59·23%; H=5·47%; $C_{15}H_{17}O_4N_3$ requires C=59·4%; H=5·6%).

The *semicarbazone of the ethyl ester* crystallised from alcohol in yellow needles m.p. 208°C. (decomp.) (Found: C=61·51%; H=6·25%; $C_{17}H_{21}O_4N_3$ requires C=61·63%; H=6·34%).

The neutral compound from the above chalkone-acetic acid.—This was obtained by treating the chalkone-acetic acid m.p. 232° (2 g.) with concentrated sulphuric acid (10 c.c.) at a temperature of 60° C. for 1 hour. The precipitate obtained on pouring the resulting fluorescent solution in water gradually became granular on keeping for few hours. It was filtered, treated with dilute sodium carbonate solution, and the insoluble portion was crystallised from methyl alcohol in rectangular plates m.p. 165° C. yield 1·5 g.

(Found : C=75·5% ; H=6·46% ; $C_{23}H_{24}O_4$ requires C=75·8% ; H=6·6%).

The *semicarbazone* was obtained by refluxing the neutral compound in alcoholic solution with the reagents for 3 hours, and crystallised from alcohol in parallelogramic plates m.p. 245° C. (decomp.) (Found : C=63·2%; H=6·3% ; monosemicarbazone $C_{24}H_{27}O_4N_3$ requires C=68·4% ; H=6·4% ; disemicarbazone $C_{25}H_{30}O_4N_6$ requires C=62·76% ; H=6·28%).

Action of sulphuric acid on the monolactonic acid m.p. 205° C. : *Formation of the dilactone of ββ′-(22′-diethoxy-55′-dimethyl-diphenyl)-glutaric acid.*—The recrystallised monolactonic acid (5 g.) was dissolved in concentrated sulphuric acid (20 c.c.) and the solution heated at a temperature of 60° C. for one hour. On pouring in 100 c.c. of ice water and keeping overnight, the crystalline precipitate which separated was filtered and treated with boiling dilute sodium carbonate. The sodium carbonate filtrates on acidification gave the 6-methyl-coumarin-4-acetic acid (yield 1 g.) m.p. 180° C. (decomp.). The neutral dilactone insoluble in sodium carbonate was washed with water and crystallised from 100 c.c. methyl alcohol in colourless pyramids m.p. 184° C. (yield 3 g.) (Found : C=73·90% ; H=5·14% ; $C_{19}H_{16}O_4$ requires C=74·00% ; H=5·2%). Action of 80% sulphuric acid on the monolactonic acid overnight produced only the 6-methyl-coumarin-4-acetic acid, and no neutral dilactone. The dilactone slowly went in solution in boiling caustic alkalies, which on acidification carefully after cooling in ice gave an acid, which decomposed at 110° C. and produced the original dilactone. This acid gave intense phenolic colouration with ferric chloride in cold alcoholic solution which disappeared on warming. All the attempts to purify this acid were rendered futile, each time the dilactone being the resulting product.

Hydrolysis and ethylation of the dilactone m.p. 184° C. : *Formation of ββ′-(22′-diethoxy-55′-dimethyl-diphenyl)-glutaric acid.*—The neutral dilactone (1·5 g.) was finely powdered and refluxed with (30 c.c.) of 25% sodium hydroxide solution, when it gradually dissolved. The pale yellow solution was filtered and heated on a small flame just to boiling, while freshly distilled diethyl-sulphate (6 c.c.) was gradually run in during about 20 minutes; shaking the reaction mixture at frequent intervals. The resulting liquid was refluxed for 15 minutes, when the diethyl ester of the glutaric acid separated as a yellow oil, which solidified to a colourless crystalline mass on cooling to the room temperature. It was filtered, dried in a vacuum over calcium chloride, and crystallised from methyl alcohol, obtaining thus (1·2 g.) of colourless parallelogramic plates m.p. 82° C. Hydrolysis of the diethyl ester with alcoholic potash furnished the glutaric acid which crystallised from alcohol in colourless parallelogramic plates, m.p. 219° C.

(decomp.). Some more of the glutaric acid was obtained by cooling the above alkali filtrates in ice, when its sodium salt separated as colourless silky needles. These were filtered, treated with boiling dilute hydrochloric acid for a while, again filtered, washed with water, and taken up in dilute sodium carbonate solution. Any undissolved neutral product was filtered out and the solution acidified, thus giving (0·5 g.) more of the glutaric acid. The glutaric acid is soluble in acetone and acetic acid, sparingly so in alcohol or ethyl acetate and insoluble in water, petrol, or benzene. It gave an insoluble barium salt in cold (Found: C=68·92%; H=6·96%; Eq=201; $C_{23}H_{28}O_6$ requires C=69·00%; H=7·00%; Eq=200. Found: Ba=25·2%; $C_{23}H_{26}O_6Ba$ requires Ba=25·6%).

The glutaric acid, by warming with concentrated sulphuric acid, gave a mixture mainly of the dilactone m.p. 184° C. and 6-methyl-coumarin-4-acetic acid, with a small amount of the monolactonic acid m.p. 205° C. Similarly the monolactonic acid (2 g.) by hydrolysis and ethylation with 25% sodium hydroxide (25 c.c.) and diethyl sulphate (5 c.c.) gave the glutaric acid m.p. 219° C. (decomp.).

The *diethyl ester* could also be prepared from the glutaric acid by alcohol and sulphuric acid (Found: C=70·8%; H=7·8%; $C_{27}H_{36}O_6$ requires C=71·00%; H=7·90%).

The *dimethyl ester* crystallised from methyl alcohol in colourless flat needles, m.p. 105° C. (Found: C=69·90%; H=7·4%; $C_{25}H_{32}O_6$ requires C=70·10%; H=7·47%).

Unlike the glutaconic acids, these glutaric esters do not condense with aromatic aldehydes. On condensing the dimethyl ester (1 mol.) with dimethyl oxalate (3 mols.) in the presence of sodium methoxide, according to Dieckemann's method,[7] most of it was recovered unchanged. Very small amount of a substance melting above 160° C. was however obtained as a more soluble fraction, which on further examination appeared to be a complex mixture.

The *anhydride* was prepared from the glutaric acid by the action of acetic anhydride or by thermal decomposition at 220° C. temperature. It crystallised from benzene in colourless flat rods, m.p. 189° C. It is insoluble even in caustic alkalies, and does not give any colouration with ferric chloride in cold alcoholic solution: (Found: C=72·08%; H=6·73%; $C_{23}H_{26}O_5$ requires C=72·25%; H=6·8%).

The *acid-anilide* of the glutaric acid was prepared from the above anhydride and aniline in benzene solution, and crystallised from 80% alcohol in colourless silky needles m.p. 193° C. (decomp.) (Found: C=73·00%; H=6·7%; $C_{29}H_{33}O_5N$ requires C=73·24%; H=6·9%).

The *anil* is formed by the action of aniline on the glutaric acid at a temperature of 220° C. or by the decomposition of the above acid anilide at its melting point. It was crystallised from alcohol in colourless rectangular prisms m.p. 216° C. It is insoluble in even boiling caustic alkalies and does not give any colouration with ferric chloride (Found: C=75·91%; H=6·62%; $C_{29}H_{31}O_4N$ requires C=76·15%; H=6·78%).

ββ'-(22'-dimethoxy-55'-dimethyl-diphenyl)-glutaric acid.—This dimethoxy acid corresponding to the diethoxy, could not be had either in the condensation of *p*-cresol-methylether with acetone-dicarboxylic acid, or by condensing the β-(2-methoxy-5-methyl-phenyl)-glutaconic acid with *p*-cresol-methylether (see below). This glutaric acid was however prepared from the above dilactone m.p. 184° C. by hydrolysis and methylation. The compound crystallised from alcohol in colourless rectangular prisms, m.p. 192° C. (decomp.). It gave an insoluble barium salt in cold (Found: C=67·62%; H=6·38%; Eq.=188; $C_{21}H_{24}O_6$ requires C=67·74%; H=6·45%; Eq.=186).

Condensation of p-*cresol-methylether with acetone-dicarboxylic acid* (improved method).—Finely powdered citric acid (200 g.) was mixed with concentrated sulphuric acid (200 c.c.) and fuming sulphuric acid (20% SO_3, 120 c.c.) was later added. The mixture was shaken well and heated on a water bath at 60° C. temperature till the evolution of carbon monoxide stopped and a clear orange solution was obtained. This was cooled in a freezing mixture, *p*-cresol-methylether (80 c.c.) gradually added with shaking and the reaction mixture, on standing for 3 hours, poured over 800 g. of crushed ice. The thus separated sticky solid became crystalline on keeping overnight, was then filtered, and treated with dilute sodium carbonate solution to remove any unchanged *p*-cresol-methylether, when on acidification 52 g. of mixed acids were obtained. This was treated with boiling 10% acetic acid (1000 c.c.) and filtered, when the filtrate on cooling deposited crystals of the β-(2-methoxy-5-methyl-phenyl)-glutaconic acid. The glutaconic acid crystallised from water in colourless rectangular plates m.p. 167° C. (decomp.). Gogte and Limaye[8] give the m.p. 169° C. (decomp.).

22'-dimethoxy-55'-dimethyl-chalkone-α-acetic acid.—The portion insoluble in acetic acid in above, was crystallised from alcohol. This was dissolved in least amount of boiling 10% sodium carbonate solution, which on cooling deposited the sodium salt of the chalkone-acetic acid as colourless leaflets. These were collected at the pump under strong suction, acidified with hydrochloric acid, and the chalkone-acetic acid thus obtained was recrystallised from alcohol in colourless parallelogramic plates, m.p. 252° C. yield 12 g. The acid is a remarkably stable compound being unchanged even on fusion

with solid potash. It is soluble in acetone, sparingly so in acetic acid or alcohol, and insoluble in other organic solvents. It gave an insoluble barium salt in cold. Its ethyl ester did not condense with aromatic aldehydes (Found : C=71·00% ; H=6·13% ; Eq.=346 ; $C_{21}H_{22}O_5$ requires C=71·2%; H=6·2% ; Eq.=354. Found : Ba=15·6% ; $(C_{21}H_{21}O_5)_2Ba$ requires Ba=16·25%).

*The *ethyl-ester* crystallised from 70% methyl alcohol in parallelogramic plates m.p. 122° C. (Found : C=72·1% ; H=6·7% ; $C_{23}H_{26}O_5$ requires C=72·24% ; H=6·8%).

*The *semicarbazone* was obtained by refluxing the alcoholic solution of the chalkone-acetic acid with semicarbazide hydrochloride and sodium acetate for 4 hours. When recrystallised from alcohol, it melted at 277° C. (decomp.) (Found : C=64·00% ; H=5·92% ; $C_{22}H_{25}O_5N_3$ requires C=64·24% ; H=6·08%).

*The *semicarbazone of the ethyl-ester* crystallised from alcohol in colourless needles m.p. 219° C. (decomp.) (Found : C=65·38% ; H=6·44% ; $C_{24}H_{29}O_5N_3$ requires C=65·6% ; H=6·6%).

Synthesis of the chalkone-acetic acid m.p. 252° C. *from* β-(2-*methoxy*-5-*methyl-phenyl*)-*glutaconic acid and* p-*cresol-methylether*.—The glutaconic acid (5 g.) was finely powdered and dissolved in previously ice-cooled dilute—4 vols. acid : 1 vol. water—sulphuric acid (40 c.c.). *p*-cresol-methylether (10 c.c.) was then gradually added with shaking and the whole allowed to stand overnight at the room temperature. On pouring the reaction mixture on 100 g. of powdered ice, a partly sticky mass, becoming granular on keeping for few hours, separated. It was filtered, washed, treated with 100 c.c. of boiling 10% aqueous acetic acid, and filtered. The chalkone-acetic acid insoluble in acetic acid, was purified as above. Yield 1·5 g. The acetic acid filtrates on cooling gave the 6-methyl-coumarin-4-acetic acid.

Action of sulphuric acid on the chalkone-acetic acid m.p. 252° C.—On keeping a solution of the chalkone-acetic acid (2 g.) in 80% sulphuric acid (15 c.c.) overnight at room temperature, the indone-acetic acid (1·1 g.) melting at 218° C. (decomp.), was obtained, and was found identical with that described by Gogte and Limaye.[8] Action of concentrated sulphuric acid (10 c.c.) on the glutaconic acid (2 g.) at 60° C. for 1 hour, gave on pouring the reaction mixture in water and filtering, 1·4 g. of a precipitate. It was washed with boiling water, treated with boiling dilute sodium carbonate solution and

* These three compounds had been described in the M.Sc. Thesis of the author, but the melting points of the latter two were given as 272°C., and 212°C., and their method of preparation was also different.

separated into 0·6 g. of the above indone-acetic acid and 0·8 g. of a neutral compound. This was recrystallised from 40 c.c. of alcohol in parallelogramic plates m.p. 214° C. (Found: C=74·87%; H=5·82%; $C_{21}H_{20}O_4$ requires C=75·00%; H=5·95%).

The *semicarbazone of the neutral* melted at 263° C. (decomp.) (Found: C=61·65%; H=5·6%; disemicarbazone, $C_{23}H_{26}O_4N_6$ requires C=61·30%; H=5·78%; monosemicarbazone $C_{22}H_{23}O_4N_3$ requires C=67·17%; H=5·85%).

Benzylidene derivative of the neutral.—The neutral compound was dissolved in alcohol and refluxed with benzaldehyde and alcoholic potash for one hour. Alcohol was evaporated, the residue rubbed with water to remove the alkali, and the unreacted benzaldehyde removed with steam. On crystallisation from alcohol the benzylidene compound melted at 174° C. (Found: C=78·7%; H=5·41%; $C_{28}H_{24}O_4$ requires C=79·24%; H=5·66%).

The ethyl-ester of the above chalkone-acetic acid m.p. 252° C., when treated with concentrated sulphuric acid at 50–60° C. produced the ethyl ester m.p. 158°C. of the above indone-acetic acid m.p. 218° C., mainly and a small amount of the indone-acetic acid itself, but the above neutral compound m.p. 214° C. could not be detected. Concentrated nitric acid at room temperature transformed the chalkone-acetic acid into the indone-acetic acid, and hence its oxidation with nitric acid yielded the phthalic anhydride m.p. 186° C. identical with that obtained by Limaye and Gogte[8] (*Ref.* M.Sc. Thesis of the author).

The author wishes to thank Dr. P. C. Guha, D.Sc., for the encouragement he has given and the facilities provided in carrying out the present investigation; and also to Prof. D. B. Limaye, Poona, for the helpful suggestions he gave during the progress of this work, as well as Part I of this series.

NOTE:—With regard to Part I of this series (This Journal Vol. I, No. 1, pp. 48–60) the author wishes to state the following:—The words "while working at the Ranade Institute for his M.Sc. Thesis" should be inserted after the sentence "in extending Limaye and Bhave's method" (p. 48, line 2 from bottom). The new method of synthesis of β-aryl glutaconic acids described therein, was discovered in the case of the glutaconic acids from *p*- and *m*-cresol-methylethers, during the last term of the stay of the author at the Ranade Institute, Poona, and the extension of this new method of synthesis to the glutaconic acids of the naphthol series, was carried out at the Indian Institute of Science, Bangalore.

ON THE p-POTENCY OF G (p^u-1, r).

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(Communicated by Dr. S. Chowla.)

§1. In this paper, I prove two generalisations of Wilson's Theorem and some potency properties of G (p^u-1, r). I make a free use of the results proved in an earlier paper.[3] G (n, r) denotes the sum of the products of the first n natural numbers taken r at a time. I denote by $\mathrm{G}_{a<n}(a, r)$ the sum of the products taken r at a time of all numbers less than and prime to n. p stands in general for an odd prime unless stated otherwise.

§2. *Theorem.* $\mathrm{G}[np-1, m(p-1)] \equiv (-1)^m \binom{n}{m} \pmod{p}$.

I have shown[3] that

$$\mathrm{G}(p+j, r) \equiv \mathrm{G}(j, r) \pmod{p}\ ;\ 0 \leqslant r \leqslant p-2\ ; \quad \ldots \quad \ldots \quad (3\cdot3)^4$$

and
$$\equiv \mathrm{G}(j, r) - \mathrm{G}(j, r-p+1) \pmod{p}\ ;\ r \geqslant p-1. \quad \ldots \quad (3\cdot31)^4$$

Applying these reductions k times, we get

$$\mathrm{G}[np-1, m(p-1)] \equiv \sum_{i=0}^{m} \left[(-1)^i \binom{k}{i} \mathrm{G}\{(n-k)p-1, (m-i)(p-1)\} \right] \pmod{p}.$$

Let $k = n-1$, then

$$\mathrm{G}[np-1, m(p-1)] \equiv (-1)^{m-1} \binom{n-1}{m-1} \mathrm{G}(p-1, p-1) + (-1)^m \mathrm{G}(p-1, 0) \binom{n-1}{m} \pmod{p},$$

$$\equiv (-1)^m \binom{n}{m} \pmod{p}, \text{ since}^3\ \mathrm{G}(p-1, p-1)$$

$$\equiv -1 \pmod{p}.$$

In fact, if $r \not\equiv 0 \pmod{p-1}$,
then $\mathrm{G}(np-1, r) \equiv 0 \pmod{p}$.
For, let $r \equiv s \pmod{p-1}$, $1 \leqslant s \leqslant p-2$.

Then reducing $(n-1)$ times as before, we get

$$G(np-1, r) \equiv (-1)^m \binom{n-1}{m} G(p-1, s) \pmod{p}, \text{ where } m = \left[\frac{r}{p-1}\right]$$
$$\equiv 0 \pmod{p}, \text{ since}^3\ G(p-1, s) \equiv 0 \pmod{p}.$$

In particular $G(p^u-1, r) \equiv 0 \pmod{p}$, except when $r=0$ or $\phi(p^u)$.

§3. *Theorem.* $G[p^u-1, \phi(p^u)] \equiv \pm 1 \pmod{p^u}$, $u \geqslant 1$, $p \geqslant 2$.

It is easily shown that

$$G[p^u-1, \phi(p^u)] = \underset{a<\cdot p^u}{G}[a, \phi(p^u)] + \sum_{r=1}^{p^{u-1}-1} \{p^r G(p^{u-1}-1, r). \underset{a<\cdot p^u}{G}[a, \phi(p^u)-r]\},$$

when $p \geqslant 3$, we have[2] $p^r G(p^{u-1}-1, r) \equiv 0 \pmod{p^u}$.

Hence, $G[p^u-1, \phi(p^u)] \equiv \underset{a<\cdot p^u}{\text{II}}(a) \equiv -1 \pmod{p^u}$, $p \geqslant 3$,

when $p=2$, and $u=1, 2$; $G[p^u-1, \phi(p^u)] \equiv -1 \pmod{p^u}$,

when $p=2$, and $u \geqslant 3$,

$p^r G(p^{u-1}-1, r) \equiv 0 \pmod{p^{u-1}}$, $r = 1, 2$;

$\equiv 0 \pmod{p^u}$, $r \geqslant 3$.

Moreover $\underset{a<\cdot p^u}{G}[a, \phi(p^u)-r] \equiv \left[\begin{matrix}\phi(p^u)\\ r\end{matrix}\right] \pmod{2}$,

$\equiv 0 \pmod{2}$, since $u \geqslant 3$, $r = 1, 2$.

Hence $G[p^u-1, \phi(p^u)] \equiv \underset{a<\cdot p^u}{\text{II}}(a) \equiv 1 \pmod{p^u}$, $p = 2$, $u \geqslant 3$.

Thus $G[p^u-1, \phi(p^u)] \equiv \underset{a<\cdot p^u}{\text{II}}(a)$, $p \geqslant 2$, $u \geqslant 1$; $\pmod{p^u}$.

In general $G(p^u-1, r) \equiv \underset{a<\cdot p^u}{G}(a, r) \pmod{p^u}$, $p \geqslant 3$;

and $\equiv \underset{a<\cdot p^u}{G}(a, r) \pmod{p^{u-1}}$, $p = 2$.

In particular when $r > \phi(p^u)$,

$$G(p^u-1, r) \equiv 0 \left(\text{mod. } p^{u-\left[\frac{2}{p}\right]}\right), \quad p \geqslant 2.$$

§4. Let $\omega(r)$ denote the p-potency of $G(p^u-1, r)$, $p \geqslant 3$, $r \geqslant 1$, $u \geqslant 1$. Then we have[3]

$$r\, G(p^u-1, r) = \binom{p^u}{r+1} + \sum_{k=1}^{r-1}\left[G(p^u-1, k)\binom{p^u-k}{r-k+1}\right]. \quad .. \quad (3\cdot2)^4$$

If in this equation r is given in succession the values $1, 2, 3 \ldots\ldots, p-2$, we easily prove that $\omega(r) \geqslant u$, $1 \leqslant r \leqslant p-2$. .. .. (A)

Putting $p-1$ for r, we get $\omega(p-1) = u-1$.

Again $G(p^u-1, r) = \sum_{m=1}^{r}\left[\underset{m}{f}(r)\binom{p^u}{2r-m+1}\right]$, ... $(1\cdot3)^4$

Where the f's are positive integers[1] given recursively by

$$\underset{m}{f}(r) = (2r-m)\,[\underset{m}{f}(r-1) + \underset{m-1}{f}(r-1)],\ \underset{0}{f}(r) = 0.$$

when $r \geqslant p$, it is easily proved that

$$\underset{m}{f}(r) \equiv 0 \pmod{p},\ m = 1, 2, 3, \ldots, p-4+\left[\frac{2r+4}{p+1}\right];$$

also $\underset{m}{f}(r) \equiv 0 \pmod{p},\ m = r, r-1, r-2, \ldots, r+1-\left[\frac{r-1}{p-1}\right]$.

Let β be the p-potency of the most potent of the integers

$$r+1+\left[\frac{r-1}{p-1}\right], r+2+\left[\frac{r-1}{p-1}\right], r+3+\left[\frac{r-1}{p-1}\right], \ldots, (2r+4)-p-\left[\frac{2r+4}{p+1}\right],\ r \geqslant p.$$

Then $\omega(r) \geqslant u-\beta,\ r \geqslant p$. .. .. (B)

Moreover, $2\,G(p^u-1, 2i+1) \equiv \binom{p^u-2i-1}{1} p^u\,G(p^u-1, 2i),\ i \geqslant 1,$

$\pmod{p^{>2u}}$. .. .. $(3\cdot1)^4$

Hence $\omega(2i+1) \geqslant 2u-\beta+\gamma$, ... (C)

where γ is the p-potency of $(2i+1)$, and $p^{\beta} \leqslant 4i < p^{\beta+1}$.

In particular $\omega(p^{\delta}) \geqslant 2u.\ 1 \leqslant \delta$. .. .. (D)

§5. *Theorem.* $\omega[\phi(p^{\lambda})] = u-\lambda,\ 0 < \lambda \leqslant u,\ p \geqslant 2$.

We have[3] $G(p^u-1, r) = \sum_{m=1}^{r}\left[\underset{m}{f}(r).\ \binom{p^u}{2r-m+1}\right]$, ... $(1\cdot3)^4$

where the f's are positive integers independent of p and u. Let $r=\phi(p^{\lambda})$, then the p-potency of $G(p^u-1, \phi(p^{\lambda}))$ will be definitely known if from the terms on the right-hand side of $(1\cdot3)^4$, we can single out one with a potency less than that of any and every other of the terms.

I proceed to show that such a term is

$$\underset{m}{f}(r)\binom{p^u}{p^{\lambda}},\ r=\phi(p^{\lambda}),\ m=p^{\lambda}-2p^{\lambda-1}+1.$$

Since $G[p^{\lambda}-1, \phi(p^{\lambda})]$ is 0-potent in p,

therefore $\underset{p^{\lambda}-2p^{\lambda-1}+1}{f}(r)$ is 0-potent in p; $r=\phi(p^{\lambda})$.

Moreover,

$\binom{p^u}{p^{\lambda}}$ is less potent in p than every other member of $\binom{p^u}{t}$,

where $1+\phi(p^{\lambda}) \leqslant t \leqslant 2\phi(p^{\lambda})$.

Hence $\omega\,[\phi\,(p^\lambda)]=u-\lambda,\ 0<\lambda\leqslant u.$ .. .. .. (E)

In view of the results of §3, we now get

$$\underset{a<\cdot p^u}{\mathrm{G}}\,[a,\ \phi\,(p^\lambda)]\equiv 0\ (\mathrm{mod.}\ p^{\leqslant u-\lambda}),\ p\geqslant 2,\ 1\leqslant\lambda\leqslant u. \quad .. \quad (\mathrm{F})$$

In other words $\mathrm{G}\,[p^u-1,\ \phi\,(p^\lambda)]$ and $\underset{a<\cdot p^u}{\mathrm{G}}\,[a,\ \phi\,(p^\lambda)]$, $p\geqslant 2,\ 1\leqslant\lambda\leqslant u$, are equi-potent in p.

§6. *Theorem.* $\omega\,(p^u-2)\geq\dfrac{p^u-1}{p-1}-2u+\chi,\ u\geqslant 1,$

where $\chi=1$, 2 or 3 according as $p=2$, 3, or >3.

We have $\mathrm{G}\,(p^u-1,\ p^u-2)=(p^u-1)!\sum_{a=1}^{p^u-1}\frac{1}{a}$.

$$=(p^u-1)!\left[\sum_{a<\cdot p^u}\frac{1}{a}+\frac{1}{p}\sum_{a<\cdot p^{u-1}}\frac{1}{a}+\ldots+\frac{1}{p^{u-1}}\sum_{a<\cdot p^a}\frac{1}{a}\right].$$

The theorem follows immediately from Wolstenholme's Theorem,[5] *viz.*,

$$\sum_{a<\cdot p^k}\frac{1}{a}\equiv 0\ (\mathrm{mod.}\ p^{2k-l}),$$

where $l=0$, 1, 2, according as $p=>3$, 3, or 2.

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2. . . . . "On a Theorem of Gauss," *Proc. Edinburgh Math. Soc.* (in press).
3. . . . . "Congruence Properties of G-Functions," *Proc. Edinburgh Math. Soc.* (2), 1935, **4**, 61–66.
4. These numbers refer to results obtained in 3.
5. Hansraj Gupta, "A Generalisation of Wolstenholme's Theorem," *Math. Notes, Edinburgh Math. Soc.* (in press).

IRIDIUM ISOTOPES AND THEIR NUCLEAR SPINS.

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and
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Iridium is practically the only element whose isotopic constitution has not so far been revealed by the mass-spectrograph. The present authors have arrived at the isotopic constitution of platinum from a study of the hyperfine structure of its arc lines.[1] Almost simultaneously Dempster[2] has published the isotopic analysis of this element with the aid of his mass-spectrograph. He has more recently studied the isotopes of palladium and gold,[3] whose hyperfine structure data obtained by one of us is under publication. Of the four elements, *viz.*, Pd, Ir, Pt and Au, mentioned by Aston[4] as having withstood attempts to arrive at their isotopic constitution by the use of the mass-spectrograph, iridium alone remained without any information in this respect. A study of the hyperfine structure of the arc lines of iridium was undertaken with the view of determining its isotopes as well as their nuclear spins.

The hollow cathode used in this investigation is exactly similar to the one used previously ;[5] instead of the platinum foil, an iridium sheet (supplied by Messrs. Johnson Matthey & Co., Ltd., London) was inserted in the hollow cathode. A discharge current of about 200 mA. at 1000 v. brings up the iridium arc lines arising from transitions to the low-lying levels with enough intensity to enable a study of their hyperfine structure. The advantage of the particular type of hollow cathode employed here lies in the fact that only a few lines corresponding to transitions to ground and near low-lying levels are excited without any reversal. Fig. 1 shows that in platinum as well as in iridium the lines for which the hyperfine structure study has been possible are those arising from transitions to a few of the deepest levels only. It is a matter of great advantage in hyperfine structure work to obtain such significant lines of an element intensely without any complications of self-reversal.

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[1] Venkatesachar and Sibaiya, *Nature*, 1935, **136**, 65.
[2] Dempster, *Nature*, 1935, **135**, 993.
[3] Dempster, *Nature*, 1935, **136**, 65.
[4] Aston, *Proc. Roy. Soc.*, 1935, **149**, 404.
[5] Venkatesachar and Sibaiya, *Proc. Ind. Acad. Sci.*, 1935, **1**, 955-960.

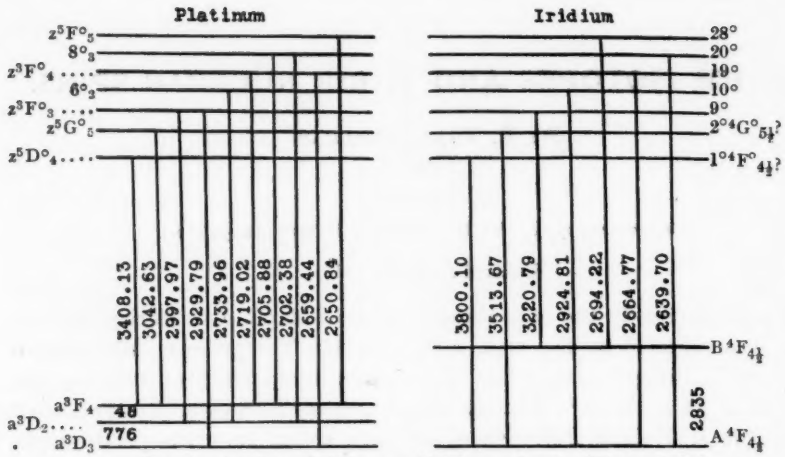


FIG. 1. Arc lines of platinum and iridium analysed. (Not to Scale.)

The spin separations even in the deepest levels of iridium are so small that many of the arc lines just appear widened and exhibit no structure. The three arc lines λλ 3800·10, 3513·67 and 2924·81 Å have a common lower level in the ground term A $^4F_{4\frac{1}{2}}$ according to Albertson.[6] These three lines exhibit similar structure; but the components are so very close together that accurate measurements have been possible only in the intense line λ 3513·67 Å. The similarity in structure and the approximate equality of the component separations suggest that the structure in these lines must be attributed to a spin splitting of the ground term A $^4F_{4\frac{1}{2}}$ with the upper levels unsplit. λ 3513·67 Å exhibits the following structure in cm.$^{-1}$ and the visual estimates of relative intensity are included in brackets:

IrI λ 3513·67 Å ($5d^86s\ ^4F_{4\frac{1}{2}} - 5d^86p\ ^4G^0_{5\frac{1}{2}}$)

dν in cm.$^{-1}$ (Int.)	Remarks
+0·072 (7)	This component appears as a continuous patch between +0·072 and 0·000, indicating the presence of an expected satellite at +0·033 (9), *vide* Pl VIII.
0·000 (22)	Broad.
−0·073 (13)	
−0·145 (9)	

[6] Albertson, *Phys. Rev.*, 1932, **42**, 443.

Judging from the known isotopic constitution of elements with odd atomic numbers, iridium can have either *one* or *two* odd isotopes. If one assumes the existence of only one isotope, the chemical atomic weight 193·1 suggests that the isotope is Ir 193. No value of nuclear spin for Ir 193 even with the lower and upper levels both split can give the observed structure; this fact has been established by the method of Fisher and Goudsmit employed for explaining the structure of insufficiently resolved lines. Another alternative is that iridium should consist of two isotopes Ir 193 and Ir 195, because the chemical atomic weight is 193·1. Examining all the known odd isotopes of elements, it is found that 191 and 193 are the only two odd mass numbers missing in the neighbourhood of iridium; 195 has been previously shown to exist in platinum.[1,5] It appears further that the isotopes of an element with odd atomic number usually have no isobars in appreciable quantity. Since the isotope of mass 195 exists to an extent of about 30% in platinum,[7] the existence of Ir 195 in any quantity is very improbable. Remembering that no element with odd atomic number exhibits more than two odd isotopes, one need only consider 191 and 193 as the isotopes of iridium. Examining the data on the atomic weight determinations of iridium, it is found that there is great divergence in the values given by various investigators ranging from 192·59 to 193·40. In these circumstances much importance cannot be attached to the value of the atomic weight 193·1. In many cases where the mass-spectrograph has decided against the chemical atomic weight as in Tb, Tm, Au, Ta, etc., the chemical atomic weight has been in excess of the true value. The observed structure of the lines is accounted for uniquely by assuming the existence of the two isotopes 191 and 193 with the respective nuclear moments of $\frac{1}{2}\frac{h}{2\pi}$ and $\frac{3}{2}\frac{h}{2\pi}$. The

$\Delta i=0$			$\Delta i=\pm 1$				
		i			i		i
Cl	35, 37	$\frac{3}{2}$					
Cu	63, 65	$\frac{3}{2}$	Hg	199	$\frac{1}{2}$	Hg 201	$\frac{3}{2}$
Ga	69, 71	$\frac{3}{2}$					
Br	79, 81	$\frac{3}{2}$	Rb	87	$\frac{3}{2}$	Rb 85	$\frac{5}{2}$
Cd	111, 113	$\frac{1}{2}$					
Sn	117, 119	$\frac{1}{2}$	Sb	121	$\frac{5}{2}$	Sb 123	$\frac{7}{2}$?
Ba	135, 137	$\frac{3}{2}$					
Eu	151, 153	$\frac{5}{2}$	Xe	129	$\frac{1}{2}$	Xe 131	$\frac{3}{2}$
Re	185, 187	$\frac{5}{2}$					
Tl	203, 205	$\frac{1}{2}$	Ir	191	$\frac{1}{2}$	Ir 193	$\frac{3}{2}$

[7] Venkatesachar and Sibaiya, *Proc. Ind. Acad. Sci.*, 1935, **2**, 101-103.

addition of two neutrons to the nucleus of the odd isotope of lower mass gives rise to an odd isotope of heavier mass with a change in nuclear spin of either 0 or ± 1; the change is 0 when the two added neutrons have opposite spin moments and is ± 1 when their spins have the same sign. Tamm and Altschuler[8] also consider that sometimes two neutrons do not form a closed shell with zero spin, but add up to give a spin of 1. The above table contains all the known cases where the nuclear spin change between two odd isotopes of an element is either 0 or ± 1.

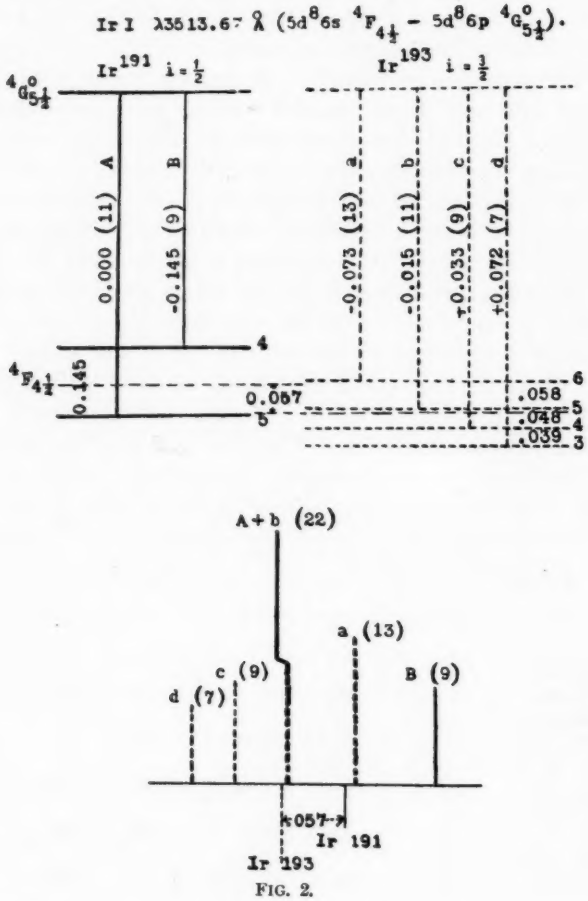
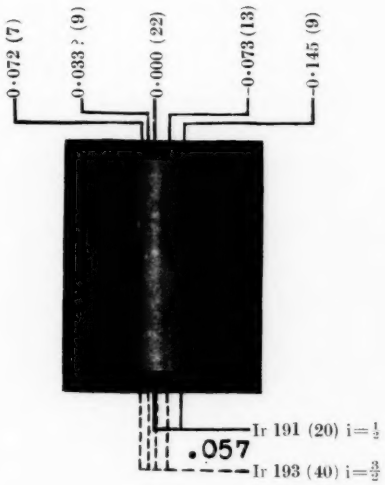


FIG. 2.

[8] Tamm and Altschuler, *"Ac"*, *U.R.S.S.*, 1934, **1**, 455.


0·072 (7)
0·033 ? (9)
0·000 (22)
-0·073 (13)
-0·145 (9)
Ir 191 (20) i=½
.057
Ir 193 (40) i=3/2

The observed structure of λ 3513·67 Å is explained on the basis of two isotopes 191 and 193 with nuclear spins of $\frac{1}{2}$ and $\frac{3}{2}$ respectively in Fig. 2. The eye-estimates of the intensities of the components is consistent with theoretical expectations and give for the relative abundance of the isotopes 191 and 193 a ratio approximately equal to 1 : 2. The correct ratio however must await a microphotometric study of the structure pattern. The above estimate gives an atomic weight of 192·4, which is perhaps a little too low. There is no doubt however that the accepted chemical atomic weight is too high, and that the correct atomic weight of iridium must lie between 192 and 193. An accurate estimate of the relative abundance of the isotopes is further impeded by the uncertainty of the J-value of the ground term; Meggers and Laporte give it as $2\frac{1}{2}$ while Albertson gives it as $4\frac{1}{2}$. The ground term exhibits an isotope displacement of 0·057 cm.$^{-1}$ with the heavier isotope lying deeper as in the cases of copper and thallium.[9] The existence of this isotope shift favours the suggestion that the ground term of iridium is a $^4F_{4\frac{1}{2}}$ term as suggested by Albertson arising from an electronic configuration $5s^25p^65d^86s$ in preference to a $^2D_{5/2}$ term from $5s^25p^65d^9$ as given by Meggers and Laporte[10]. It is for this reason that the J-value of the ground term has been here assumed as $4\frac{1}{2}$ in calculations of intensity, intervals and isotope shift. The incompletely resolved patterns of a few other IrI lines 3220·79, 2694·22, 2664·77 and 2639·70 support the conclusions obtained above regarding the isotopes of iridium and their nuclear spin. The fine structure levels in $B^4F_{4\frac{1}{2}}$ of Albertson are regular in Ir 191 and inverted in Ir 193, while in $A^4F_{4\frac{1}{2}}$ the reverse is the case. The ratio of the nuclear magnetic moments of the two isotopes is therefore about −1·0.

Summary.

The hyperfine structure patterns of some of the significant arc lines of iridium have been photographed using as source a hollow cathode tube already described in a paper by the authors on the isotopic constitution of platinum. An examination of the hyperfine structure data of the iridium lines leads to the result that it consists of two isotopes with nuclear spins $\frac{1}{2}\frac{h}{2\pi}$ and $\frac{3}{2}\frac{h}{2\pi}$. A consideration of known facts regarding the occurrence of isotopes of different mass numbers in the various elements has led to the inference that the mass numbers of the two iridium isotopes are 191 and 193 with a relative abundance of nearly 1 : 2, the isotope with the higher mass number having the higher nuclear spin.

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[9] Venkatesachar and Sibaiya, *Proc. Ind. Acad. Sci.*, 1934, **1**, 13.

[10] Meggers and Laporte, *Phys. Rev.*, 1926, **28**, 660.

1126-35.—Printed at The Bangalore Press, Bangalore City, by T. Subramania Aiyar, Superintendent,
and Published by The Indian Academy of Sciences Indian Institute of Science, Bangalore.

FLUORESCENCE IN CYCLOHEXANE.

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction.*

While investigating the polarisation of light-scattering in cyclohexane for different wavelengths an intense continuous spectrum in the region 2700–4000 Å was found to have developed after long exposures which interfered with the depolarisation measurements. A study of this fluorescence was therefore taken up in order to ascertain its cause so that it could be avoided if possible. It was found that Haberl[1] had noticed this phenomenon a few months earlier and had arrived at certain conclusions regarding the nature and origin of the fluorescence in cyclohexane. Since the observations of the author do not agree with those of Haberl and lead to entirely different results it has been thought worthwhile to publish them.

2. *Experimental.*

The apparatus used for the investigation was made completely of silica and consisted of a distilling flask to which a tube closed at both ends was attached. The requisite amount of pure cyclohexane was introduced into the apparatus which was then evacuated and sealed off. After repeated distillations the pure dust-free liquid which collected in the tube was used for the work. The light from a quartz mercury point source lamp was focussed on to its side with a quarter condenser and the light scattered at right angles was examined with a quartz spectrograph (dispersion: 40 Å per m.m. at $\lambda = 4000$ Å).

3. *Preparation of Pure Cyclohexane.*

250 gms. of cyclohexane (T. Schuchardt) labelled as "pure" were agitated thoroughly with oleum for 10 hours on a shaking machine, washed repeatedly with a dilute suspension of precipitated chalk and then with distilled water after which it was distilled twice over anhydrous calcium chloride in an all-glass apparatus using a Widmer-Schenck column for fractionation. The boiling point was steady at 77° (pressure = 680 m.m.). The middle fraction was used for the experiment.

[1] *Ann. der Physik.*, 1934, **21**, 301.

4. Nature of the Fluorescence Spectrum.

According to Haberl (*loc. cit.*) the fluorescence band has two maxima at $\lambda = 2900$ Å and 4000 Å respectively, the latter being nearly as intense as the scattered 4046 line of mercury. The phenomenon, according to him, is constant and reproducible, while long irradiation with a mercury arc has no influence. The present observations, however, point to a wholly different conclusion. For example, it was noticed at the outset that, under identical conditions, such as time of exposure, intensity of incident light, etc., the fluorescence spectrum varied from experiment to experiment. At first only a feeble continuous spectrum from 2700–2900 Å was observed but with successive exposures the intensity increased while the spectrum gradually extended towards the side of longer wavelengths. After illuminating the substance for 8 hours with a quartz mercury arc, it was noticed that the light track, barely perceptible before, was now clearly visible. The fluorescence band was also found to have extended into the visible spectrum and although in the absence of a microphotometric record the exact positions of the maxima could not be located, there appeared to be a rough agreement with the results of Haberl. It appears therefore that his picture of the fluorescence spectrum has been obtained with a sample which had been strongly illuminated with ultraviolet light. His experimental arrangement in which a large mercury arc is placed alongside the tube containing the substance[2] is quite in contrast to the feeble mercury point source (about 2 amperes at 10 volts) used in the present work and supports such a conclusion. The strong fluorescence in the irradiated substance was found to be completely removed by distilling it twice or thrice indicating thereby that the constituents responsible for the fluorescence are non-volatile.

5. Is Fluorescence a Characteristic of Pure Cyclohexane?

The above observations suggest that, on exposure to the ultraviolet, some photochemical decomposition takes place and the products of decomposition give rise to the observed fluorescence. This is further illustrated by the following experiment :—Two pictures of the fluorescence spectrum were taken on a single plate, the first with an exposure-time of one hour while the second was taken with four exposures of 15 minutes each, the liquid being distilled afresh after every exposure. The intensity of the fluorescence was distinctly greater in the former case. In order to decide definitely whether the fluorescence could be wholly ascribed to the products of photochemical action, an apparatus was designed (Fig. 1) in which the

[2] Haberl, *Ann. der Physik.*, 1934, **21**, 301.

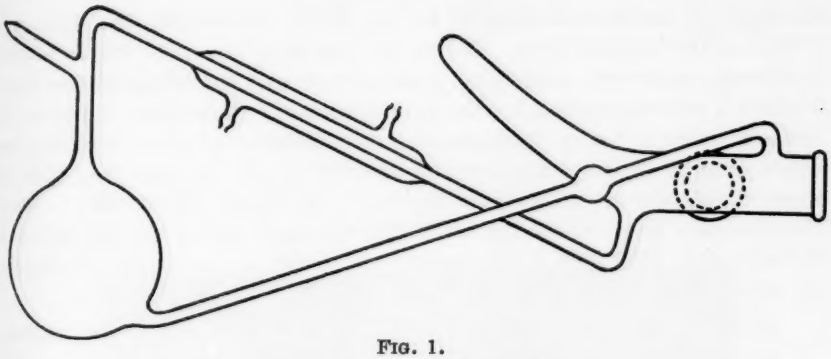

FIG. 1.
Apparatus for Continuous Distillation.

substance could be continuously renewed by distillation. The arrangement of Pal and Sen Gupta[3] was first tried but was not found to work satisfactorily on account of two reasons: (1) The inlet and outlet tubes are both situated on the upper side and hence only the top layer of the liquid is renewed, the main bulk of the liquid remaining unchanged. (2) The distilling flask being at a lower level, the liquid siphons out intermittently from the tube. In the apparatus illustrated above, these difficulties have been avoided (1) by placing the inlet on the under surface of the tube and (2) by blowing a small bulb on the outlet tube so as to avoid the siphoning action. If the distilling vessel is kept immersed in hot water, liquid enters and flows out of the tube in a continuous stream. The apparatus was made of pyrex glass except for the two quartz windows which were stuck on with a solution of sodium silicate. It was found that, with this arrangement, even an exposure of 6 hours, did not show any continuous spectrum on the plate (Fig. 2). A picture taken without the substance being renewed by continuous distillation is also shown side by side for comparison. The contrast is clearly noticeable. This experiment furnishes definite proof that pure cyclohexane has no fluorescence at all.

6. *Origin of the Fluorescence.*

It became of interest now to examine what wavelengths are photochemically active in the above reaction. According to Haberl, the interposition of a thin glass plate in the path of the incident light which cuts off all wavelengths less than $\lambda=3000$ Å removes the fluorescence completely. He concludes therefrom that the resonance line $\lambda=2537$ Å is perhaps responsible for the fluorescence. A picture was taken with a filter of 1 cm.

[3] *Ind. Jour. Phys.*, 1930, **5**, 609.

thickness of carbon tetrachloride to cut off all wavelengths less than $\lambda=2600$ Å in the incident light. The picture obtained was quite free from any continuous spectrum, suggesting thereby that only wavelengths less than $\lambda=2600$ Å were responsible for the decomposition.* A similar experiment, however, using a 5 m.m. thickness of 2 molal solution of acetic acid as filter which absorbs all wavelengths transmitted by quartz but less than 2400 Å[4] shows the fluorescent spectrum with almost undiminished intensity. Since the resonance line $\lambda=2537$ Å is by far the strongest line of the mercury arc in the region 2400–2600 Å this wavelength seems to be largely responsible for exciting the fluorescence spectrum.

Further work on the nature of the photochemical reaction is in progress.

In conclusion, the author wishes to express his grateful thanks to Sir C. V. Raman, Kt., F.R.S., N.L., for his valuable help and guidance during the progress of this investigation.

Summary.

(1) An apparatus for continuous distillation has been described which works satisfactorily and is free from the defects of the arrangement described by Pal and Sen Gupta.[5]

(2) With the help of the above apparatus pure cyclohexane is shown to have no fluorescence; that reported by Haberl[6] has been proved to be due to products of photochemical decomposition.

(3) The wavelengths in the region $\lambda=2400$–2600 Å have been found to be active in the above reaction.

* Contrary to the observations of Haberl, in the case of cyclohexane which had been exposed to the mercury arc for some time, the fluorescence in the visible is not removed by introducing a glass plate in the path of the incident light. The intensity of the fluorescence, however, is somewhat diminished as can be seen from the photographs (Figs. 3 and 4). This shows the necessity for distinguishing between wavelengths responsible for photochemical action and wavelengths capable of exciting fluorescence.

[4] Kishakowsky and Nelles, *Phys. Rev.*, 1932, **41**, 595.

[5] *Ind. Jour. Phys.*, 1930, **5**, 609.

[6] *Ann. der Phys.*, 1934, **21**, 301.

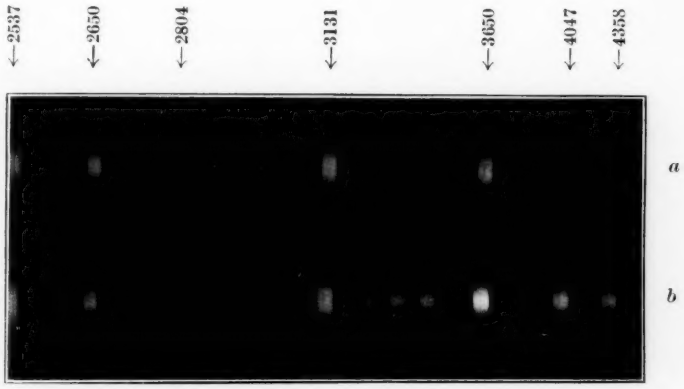

FIG. 2.

(*a*) With continuous distillation.
(*b*) Without continuous distillation.

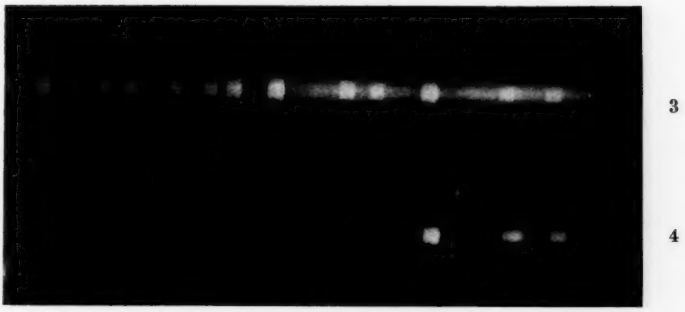

FIG. 3. Fluorescence spectrum of irradiated cyclohexane, exposure 2 hours.

FIG. 4. Fluorescence spectrum with glass plate in the path of the incident light, exposure 2 hours.

THE DENSITY AND COMPRESSIBILITY OF SILICANE AND SILICOETHANE.

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and
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Received August 3, 1935.
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

In connection with work previously published on the dielectric coefficients of gases,[1] approximate measurements of compressibility at different temperatures were required. Density determinations for the purpose of checking the purity of the gases were also desirable and consequently the apparatus now to be described was erected, the design being due to Dr. H. E. Watson.

Among the gases examined were silicane and silicoethane, the densities of which appear to have been measured only by Stock and Somieski,[2] who gave the values 32·29 and 63·8 or 64·2, as compared with $O_2=32$. No attempt was made by these authors to deduce the atomic weight of silicon as the compressibilities were not determined. Silicane is a gas which can be prepared in a state of considerable purity without great difficulty and the results of the present series of experiments are recorded as indicating that, with a few additional refinements, the density method would be suitable for an accurate determination of the atomic weight of silicon.

Apparatus.

The essential features of the apparatus consisted of a density bulb which could be detached and weighed, and a second bulb of known volume into which the gas could expand, so that the pressure of a given quantity could be determined at two different volumes. Details are shown in Fig. 1. *A* is the density bulb made of pyrex glass with a long calibrated capillary stem closed by the tap *T* and fitted with a ground conical end. The joint was made gas-tight with a very little apiezon grease, which did not appear to be attacked by the gas. *B* is a small bulb to condense the gases and fractionate them when necessary. *M* is a cylindrical bulb with its ends made from two pieces of the same tubing from which the manometer, M_1,

[1] *Proc. Roy. Soc.*, 1934, **143A**, 558.
[2] *Ber.*, 1916, **49**, 1, 111.

is constructed. In these ends are fixed two glass points, P and P_1, to which, the mercury meniscus can be set. The volume of M is approximately the

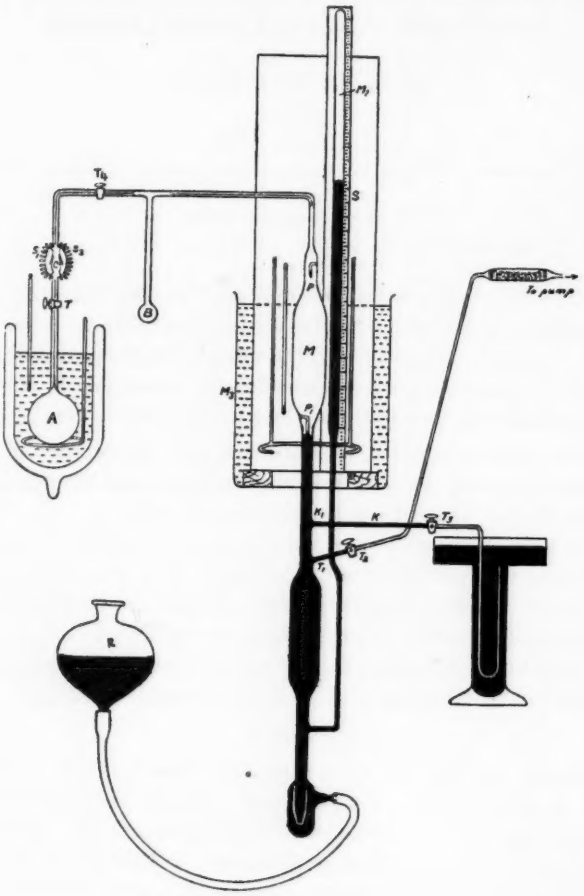

FIG. 1.

same as that of A. At T_1, a side tube with a tap T_2 connects the apparatus to a Toepler pump. Gas can be introduced through the syphon K and tap T_3.

All the apparatus except the density bulb was made of durosil glass. M was surrounded with a glass water jacket and the manometer was enclosed in a box with plate glass sides to protect it from draughts.

Calibrations.

The calibration of the apparatus was done before assembly. The volume of the density bulb A and the change with temperature were determined, using air-free distilled water. The change of volume with pressure was found by noting the increase in the height of level of water in the capillary stem by a known decrease of pressure.

A pyrex counterpoise was constructed with the same weight and external volume as the density bulb. These were checked by finding the loss of weight in water.

The volume of M between the points $P \ldots . P_1$ was determined by attaching a tap at the bottom and weighing the amount of distilled mercury required to fill it and the dead space and other parts of the apparatus were calibrated in a similar manner. The thermometers, thermocouples and the weights were all calibrated in the usual way.

All pressure readings were reduced to 0° and 45° lat. at sea level and corrected for meniscus height. The glass scale by the Société Genevois was checked against a standard invar scale.

Experimental Procedure.

After attaching the density bulb to the apparatus as shown in Fig. 1, the entire apparatus was evacuated thoroughly. The gas was then introduced and fractionated if necessary. When measurements had to be made at ordinary temperatures, the baths for the density bulb and the bulb M were adjusted to the same temperature as that of the room. At other temperatures, the necessary low-temperature bath was used only for the density bulb A. Sufficient time was allowed for equilibrium to be attained. A thin layer of paraffin oil was spread over the surface of the water in M_3 to minimise the loss of heat due to evaporation.

When the pressure was steady, the level of mercury was adjusted to the pointer P_1 with the meniscus rising. The pressure, meniscus heights, the temperature of the dead space and the temperatures of the two baths were then read. Next, the level of the mercury was adjusted to the pointer P and similar readings were taken. This was repeated several times.

Before measuring the density, it was found advisable to test the gas for traces of hydrogen by cooling B in liquid air and evacuating. After the removal of any trace of hydrogen present, B was placed in water at room temperature and the temperatures and pressure read as soon as they were steady. The tap T was then closed, the gas in the dead space was condensed in the bulb B and the tap T_4 was closed.

The bulb was removed and the grease washed off with ether. After drying, it was placed in the balance along with the counterpoise, which had been subjected to similar treatment. Several hours were allowed to elapse before weighings were made. As in the case of the calibration of weights, the interchange method was employed when weighing the gases, the sensitiveness being determined in each case. The weight of the empty bulb was taken both before and after the experiments, and it was found that no measurable change occurred. This indicated that the gas did not decompose in the interval.

The necessary corrections for the weight, volume, pressure and temperature were applied and the density calculated.

Compressibility.

The apparatus may be considered to consist of three parts, (1) the density bulb, (2) the dead space, (3) the expansion bulb M. If it be assumed that the compressibility is linear, *i.e.*, $pv = p_\circ v_\circ (1 - Ap)$, the mass of gas in a volume v, at a pressure p, is proportional to $\frac{pv}{(1-Ap)T}$, where T is the absolute temperature.

Denoting by suffixes the volumes and temperatures of the three parts, and, by a dash, corresponding quantities at a second observation, the general equation—

$$\frac{pv_1}{(1-A_1p)T_1} + \frac{pv_2}{(1-A_2p)T_2} + \frac{pv_3}{(1-A_3p)T_3} = \frac{p'v'_1}{(1-A'_1p')T'_1} + \frac{p'v'_2}{(1-A'_2p')T'_2} + \frac{p'v'_3}{(1-A'_3p')T'_3}$$

holds good, since the pressure throughout the apparatus is constant. In practice, this admits of considerable simplification : v_2 is small and equal to v'_2, while T_2, T_3, T'_2 and T'_3 are very nearly equal so that A_2, A_3, A'_2 A'_3 may be considered equal.

When the compressibility is determined at room temperature in the manner already described, p is the pressure with the mercury at the point P_1, and p' when it is raised to P. v'_3 is consequently zero ; the temperatures are all nearly the same and all the A terms are equal to, say, A_T. A_T may, therefore, be determined, all the other quantities being known. On repeating the experiment with the bulb cooled, T_1 and T'_1 are unequal and, consequently, so are A_1 and A'_1—say, A'_T. Since A_T is now known, A'_T may be calculated.

The compressibility at low temperature may also be determined by raising the mercury to the upper point and then cooling the density bulb

and reducing the pressure simultaneously to keep the volume constant. This method has the advantage that v_3, v'_3 are both zero and hence the result is not affected by a calibration error in this part of the apparatus ; on the other hand, the temperature T'_1 must be known with greater accuracy than in the other method.

Preparation and Purification of Materials.

The silicon hydrides were prepared by the method recommended by Stock and Somieski.[3] Magnesium silicide was made by the ignition of a mixture of anhydrous silica free from alkali, and magnesium turnings free from arsenic and phosphorus, Kahlbaum's analytical reagents being used for the purpose. The silicide was then powdered, sieved and the excess of unburnt magnesium removed mechanically. About 25 grams of this product were then decomposed in an atmosphere of hydrogen by adding it gradually to a ten per cent. solution of pure hydrochloric acid, the temperature being kept in the neighbourhood of 50° C.

The evolved gas after passing through a reflux condenser, a spray trap and a U tube at −10° C., was condensed in a U tube cooled by liquid air and the major portion later boiled off into a gas holder. The gas was recondensed and pumped off at a temperature of about −155° C., the vapour pressure being 30 millimetres. At this temperature the vapour pressure of Si_2H_6 according to Stock is less than 0·1 mm. As soon as the pressure fell to 1—2 mm., the bath was replaced by one of solid ether (−115°) and pumping continued until the pressure reached 2 mm. which is just above the vapour pressure of Si_2H_6 at that temperature. On raising the temperature to −90° C. more gas was removed consisting mainly of Si_2H_6. This fractionation was repeated several times until the gases appeared fairly pure.

Preliminary density measurements gave high values for SiH_4 and these were ascribed to the presence of carbon dioxide. This was removed by inserting into each tube containing the gas a small piece of freshly prepared quicklime which did not attack the silicane at an appreciable rate. The gas was then fractionated once more before making measurements.

Results.

The following compressibility values were obtained, each being the mean of two observations. Owing to an unfortunate accident in which most of the gas was lost, it was not possible to make measurements with Si_2H_6 at low temperatures. These values although sufficient for the purpose for which they were originally required are not accurate enough for atomic

[3] *Ber.*, 1916, **49**, 111.

TABLE I.

	t°C.	$A \times 10^3$	t°C.	$A \times 10^3$	
SiH_4 ..	27·0	7·1	24·0	8·7	
	27·0	8·4	27·5	7·9	Mean 8·4
	25·0	9·2	26·0	8·9	
	−79·8	26*	−79·8	20	Mean 23
	,,	24*	,,	21	
Si_2H_6 ..	28·0	25	27·0	26	Mean 26
	26·5	26	27·0	27	

* Constant volume method.

TABLE II.

Gas	t°C.	V c.c.	W grams	P mm.	$D_{N.T.P.}$ (Uncorr.)	$D_{P=0}$	Mol. wt.
Oxygen ..	23°·60	106·64	0·10740	581·02	1·4312	1·4302	
	24°·83	,,	0·12537	681·30	1·4307	1·4296	
Monosilane	23°·56	,,	0·12386	663·84	1·4444	1·4338	32·09
	24°·58	,,	0·12904	691·95	1·4487	1·4376	32·17
	24°·26	,,	0·12985	696·03	1·4477	1·4366	32·15
	25°·20	,,	0·12837	690·17	1·4480	1·4370	32·16
	25°·22	,,	0·12916	695·38	1·4460	1·4349	32·11
	−79°·8	106·53	0·12395	430·07	*1·4554*	*1·4348*	32·11
	,,	,,	0·12402	430·04	*1·4563*	*1·4357*	32·13
Disilane ..	28°·03	106·64	0·21312	585·16	2·8621	2·8050	62·77
	26°·95	,,	0·24819	677·50	2·8685	2·8021	62·71

Mean molecular weight of monosilane = 32·13
,, ,, disilane = 62·74

weight determinations. They could probably be improved by reading the pressures with a micrometer eye-piece instead of the simple telescope actually used, and by jacketting the manometer.

The density values are given in Table II as well as two measurements with oxygen for comparison. The values for this gas are higher than the accepted value for the normal litre 1·4290, indicating a constant error. If, however, these are taken as standard, the resulting figures for the silicanes should be fairly accurate. In the column $D_P=0$ is given the reduced density or the weight of a normal litre if the compressibility were zero. These figures are calculated from the measured density and pressure and the compressibility. The molecular weight in the last column is obtained by multiplying 32·00 by the ratio of this reduced density to that of the mean value for oxygen 1·4299.

Discussion.

Stock and Kuss[4] made some preliminary determinations of the atomic weight of silicon by the decomposition of silane with sodium hydroxide and obtained a value 28·15. Although this value was far from being decisive it suggested that the then accepted value 28·30 was rather high.

A little later Stock and Somieski[5] measured the gas densities for silicane and silicoethane and obtained the values 32·29 and 63·8 or 64·2 for the molecular weights. Apparently no corrections for the deviations from Boyle's law seem to have been applied. Assuming the values of compressibilities obtained in the present investigations to hold at the temperatures of their measurements, the values for the molecular weights work out to be 32·02 and 62·3 for mono and disilanes respectively.

Baxter and co-workers[6] from the analysis of silicon tetrachloride and tetrabromide purified by thorough fractional distillation under exclusion of air and varying pressures, obtained as the mean of a large number of determinations the value 28·063 for the atomic weight of silicon.

An year later O. Hönigschmid and M. Steinheil[7] employing the same tetrachloride method arrived at the value $28·105 \pm ·003$. At present Baxter's value has been accepted, although the relatively higher value of Hönigschmid has no reason to be rejected, being the mean of sufficiently concordant results.

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[4] *Ber.*, 1914, **47**, 3115.

[5] *Ber.*, 1916, **49**, 1, 111.

[6] *Proc. Amer. Acad. Arts and Sci.*, 1923, **58**, 245.

[7] *Zeit. anorg. Chem.*, 1924, **141**, 101.

The value obtained in the present investigations taking into consideration only the monosilane, comes out to be $28 \cdot 10 \pm \cdot 03$. This agrees practically with the value $28 \cdot 105$ given by Hönigschmid by an altogether different method. The value $28 \cdot 34$ calculated from silicoethane is undoubtedly too high owing probably to the impurities of the higher homologues and adsorption effects.

It is unnecessary to mention the several advantages of the gas density method over the other methods. It is interesting to note that the corrected molecular weights at the ordinary and low temperatures are practically the same, indicating thereby that no association occurs at low temperatures and also that the effects of adsorption of the monosilane are not appreciable.

Summary and Conclusion.

1. An apparatus for the simultaneous measurements of densities and approximate compressibilities at the ordinary and low temperatures, has been described.

2. Measurements of densities and compressibilities on monosilane at different temperatures and on disilane at the ordinary temperature have been made.

3. The atomic weight of silicon obtained from the corrected molecular weights obtained in the present investigations, has been compared with the existing values by other authors.

In conclusion we wish to express our grateful thanks to Prof. H. E. Watson for his valuable criticisms and constant interest in the work.

MOLECULAR CLUSTERING IN BINARY LIQUID MIXTURES.

(Variation with Composition and Temperature.)

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Received August 8, 1935.
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

It is well known that when certain pairs of liquids are brought together in suitable proportions, two liquid phases result; for example, in the case of phenol and water, the upper phase is a solution of phenol in water and the lower phase a solution of water in phenol. As the temperature is slowly raised, the compositions of the two phases tend to equality until at a particular temperature (called the critical solution temperature), the line of separation disappears and the whole mass presents the appearance of a single homogeneous phase. At this temperature the mixture exhibits a very marked turbidity or opalescence. The intensity of opalescence is markedly a function of temperature, being greatest at the critical solution temperature and becoming very weak as the temperature is removed from it in either direction. The earlier investigators in this field suggested as an explanation of the opalescence that the liquid mixture in the vicinity of the critical solution temperature behaves as an emulsoid. Smoluchowski was the first to propose a thermodynamic theory of the phenomenon which later was elaborated by Einstein. Einstein's formula for the intensity of opalescence received experimental support from the quantitative studies of Fürth and Zernike. There are certain features of the phenomenon, however, that do not find an explanation on the basis of the Smoluchowski-Einstein theory, one of which is that the depolarisation of the opalescence remains finite instead of tending to zero as the critical solution temperature is approached. In a recent paper[1] in these *Proceedings*, the present author presented evidence that large molecular clusters exist in such liquid mixtures in the neighbourhood of the critical solution temperature. The finite value of the depolarisation of the opalescent light arises from the fact that the size of the clusters is not small in comparison with the wave-length of light. The existence of such clusters could be demonstrated by the simple optical method developed

[1] R. S. Krishnan, *Proc. Ind. Acad. Sci.*, 1934, **1A**, 211.

by the author. This consists in examining through a double-image prism, the light scattered in the transverse horizontal direction by the mixture when it is illumined with light polarised with electric vector horizontal. If clusters of size comparable with the wave-length of light are present, the horizontal component of the scattered light would be distinctly brighter than the vertical component. In a more recent paper[2] the author has reported the results of a detailed study of the opalescence of a series of binary mixtures over a wide range of temperature above the critical point. These results fully confirm the author's preliminary report, and demonstrate the existence of clusters in liquid mixtures—not only at the critical solution temperature but also at temperatures considerably removed from it. In the present investigation, a comparative study has been made of the intensity and depolarisation of the light scattered by mixtures of phenol and water in different proportions and at different temperatures, with a view to ascertain the influence of the composition and of the temperature of the mixture on the formation of clusters. The experimental results have an important bearing on other physical properties of the mixture, such as viscosity, magnetic birefringence, etc.

2. *Experimental Details.*

For the study of the effect of composition on the formation of clusters, mixtures of phenol and water were chosen as the most suitable, as it had been found from the previous investigation that the phenomenon is most pronounced in this case. Pure crystallised phenol was melted and was mixed with pure double distilled water in the requisite proportion, and the mixture was directly transferred to a clean and dry double bulb. The double bulb was then exhausted and sealed. The mixture was then got dust-free in one of the bulbs by repeated slow distillation and washing back into the other bulb. The bulb containing the dust-free mixture was then sealed off from the other. Six different mixtures of phenol and water containing respectively (*a*) 15% by weight of phenol, (*b*) 28% of phenol, (*c*) 34% of phenol, (*d*) 50% of phenol, (*e*) 60% of phenol and (*f*) 70% of phenol, were prepared dust-free in the manner indicated. The bulbs containing these mixtures were approximately of the same capacity and the quantity of mixture contained in each was also the same.

3. *Measurement of the Depolarisation of the Scattered Light.*

The experimental arrangement employed in the present investigation was similar to that previously employed* for the measurement of the

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[2] R. S. Krishnan, *Ibid.*, 915.

* *Loc. cit.*

depolarisations ρ_u, ρ_v and ρ_h with the incident light respectively unpolarised, polarised with the electric vector vertical and with the electric vector horizontal. The ordinary lens of long focus used for condensing the light was replaced by a photographic lens of the same focal length provided with an iris diaphragm. The bulb containing the particular mixture to be studied was kept immersed in the water-bath. The temperature of the water in the bath was slowly raised and was kept steady at about 30° above the temperature of complete miscibility. The mixture was properly shaken. The depolarisations ρ_u, ρ_v and ρ_h were measured by the usual method of Cornu, with the help of a double-image prism and nicol mounted on a stand so as to be capable of independent rotation about the same axis. The mixture was then slowly cooled down and the observations were repeated for a series of temperatures up to the critical point at which the mixture separated into two layers. The errors in the depolarisation measurements arising from the background illumination were avoided by viewing the two components of the scattered light against the same background. The error due to the finite convergence of the incident beam was almost negligible since the angle of convergence was less than 3°. The values of ρ_u, ρ_v and ρ_h for various mixtures are tabulated below.

4. Intensity Measurements.

The method usually adopted by the earlier investigators in this field for the comparison and measurement of intensities of scattered light was visual photometry. Although visual photometry has been recognised as one of the accurate methods for the comparison of intensities, it is defective in that the process is tedious and at the same time subjective in nature. The advantages of using a photocell together with a direct current amplifier for comparison and measurement of feeble intensities, *e.g.*, that of light scattered by a fluid, have already been pointed out by Mr. R. Ananthakrishnan.[3] The convenience of using a photocell in such experiments lies in the fact that the state of polarisation of the light has no influence on the photoelectric current which is a direct measure of the energy of light falling on the cell. Moreover, in contrast with the visual method it is objective in nature and is less tedious. In the present investigation, therefore, the photoelectric method was employed for comparing the intensities of light scattered by the mixtures of phenol and water at various temperatures.

The experimental arrangement used for the measurement of intensity was similar to that employed for the depolarisation measurements. But the following alterations were made. The nicol and double-image prism

[3] R. Ananthakrishnan, *Proc. Ind. Acad. Sci.*, 1934, **1A**, 201.

were removed from the observation side. The transversely scattered light after passing through the side tube attached to the wooden box which contained the scattering substance was allowed to fall on the V-shaped plate of the Osram CMG 8 (gas-filled) cell manufactured by the General Electric Company, Ltd., of England. The photocell was suitably mounted inside a wooden case (well insulated) which was painted dull black. The leading tube through which the scattered light passed, was also painted dull black inside and projected into the wooden case of the photocell. The distance of the photocell from the scattering substance was about nine inches. The scattered light entering the cell was limited by a series of apertures. The whole arrangement was such that when the mixture was illumined, only the light scattered in the exact transverse horizontal direction entered the cell.

The photocell was connected to the Valve Bridge Amplifier as shown in Fig. 1.

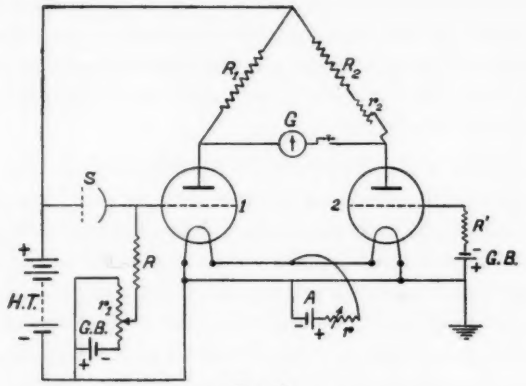

FIG. 1.

1. 2	..	L610 Marconi Dull Emitter Valves.
R_1, R_2	..	10000 ohm resistances.
R, R′	..	20 meg ohm grid leaks.
r_1	..	Varley Potentiometer (1200 ohms).
r_2	..	Adjustable rheostat (400 ohms).
r	..	Filament rheostat (5 ohms).
A	..	Filament battery (6 volts).
H. T.	..	High tension battery (115 volts).
G. B.	..	Grid bias battery (2 volts).
S	..	Osram CMG8 Photocell.
G	..	Microammeter.

This amplifier was originally set up by Mr. R. Ananthakrishnan to whom the author's thanks are due. The leads from the photocell were properly insulated to avoid disturbances in the amplifier. The amplifier was of the simplest type possible without elaborate controls and the details of its working

had already been fully described by Mr. R. Ananthakrishnan[4] in his paper on the " Photoelectric Photometry of Light Scattering in Liquids". It was found that by the use of good storage batteries, a steady state could be reached in the bridge within a short time after switching on the various connections.

The particular mixture under examination was maintained at the requisite temperature. The incident light was cut off by a chutter before it entered the mixture. The various connections in the amplifier circuit were switched on and the bridge was brought to a balance by adjusting the rheostat r_2 (see Fig. 1). The reading of the micro-ammeter was taken. The incident light was then let into the mixture and the final steady deflection of the micro-ammeter was again read off. The observations were repeated with the same mixture for a series of temperatures up to the critical solution temperature and also with the other mixtures. When the intensity of scattering was found to increase to large values as would be the case near the critical solution temperature, the intensity of the incident beam was proportionately reduced by means of the iris diaphragm attached to the long-focus lens so that the deflections of the micro-ammeter were always of the same order of magnitude.

The possible sources of error in the experiment are the following : (*a*) the want of linearity in the response of the amplifier, (*b*) the want of steadiness of the intensity of the light of the projection lantern which was used as the source of light, and (*c*) the absorption and reflections at the various surfaces. The linearity in the response of the amplifier was tested out by noting the deflections of the galvanometer using the same mixture as the scattering substance when the intensity of the incident light was reduced by known amounts. It was found that the deflections registered by the galvanometer in the bridge circuit when scattered light of a certain small intensity was allowed to fall on the photocell could be taken to be proportional to the intensity of light falling on the cell.

The intensity of light emerging out of the square aperture was measured in a foot-candle meter at regular intervals keeping the distance between the two standard carbon rods used in the projection lantern constant. It was found that the projection lantern could be taken as a fairly steady source of light within the limits of experimental error.

No account was taken of the absorption of light since the distances involved were small. In this case of the comparison of intensities, errors arising from the reflections at the various surfaces, etc., were automatically

[4] R. Ananthakrishnan, *loc. cit.*

eliminated by the use of bulbs of the same capacity for all the mixtures and by keeping the rest of the experimental arrangement undisturbed.

From the observed deflections of the micro-ammeter and from a knowledge of the proportions in which the intensity of the incident light was reduced in each case, the relative intensities of light scattered by the mixtures at various temperatures were calculated. The results are tabulated below.

TABLE I.

(*a*) 15% *Phenol.*

Temperature of the mixture °C.	ρ_h %	ρ_v %	ρ_u (observed) %	ρ_u (calculated) %	Relative intensity of transversely scattered light
88	100	1·5	3·1	3·0	1·0 (assumed)
78	100	1·1	2·3	2·2	1·3
69	100	0·75	1·4	1·5	2·0
64	100	0·55	1·1	1·1	3·8
60	100	0·5	1·0	1·0	8·3

TABLE II.

(*b*) 28% *Phenol.*

Temperature of the mixture °C.	ρ_h %	ρ_v %	ρ_u (observed) %	ρ_u (calculated) %	Relative intensity of transversely scattered light
90	100	0·9	1·7	1·8	1·0 (assumed)
87	84	0·7	1·5	1·5	1·2
81	70	0·5	1·0	1·2	1·7
77	59	0·34	0·84	0·9	2·4
74	49	0·27	0·76	0·82	3·9
72	35	0·23	0·7	0·88	5·8
68·5	22	0·15	0·62	0·83	23·8

TABLE III.

(*c*) 34% *Phenol.*

(*Critical Composition Mixture.*)

Temperature of the mixture °C.	ρ_h %	ρ_v %	ρ_u (observed) %	ρ_u (calculated) %	Relative intensity of the transversely scattered light
95	75	1·0	2·2	2·3	1·0 (assumed)
90	66	0·7	1·5	1·7	1·2
87·5	61	0·6	1·4	1·6	1·3
83	51	0·43	1·1	1·3	2·1
80	47	0·34	0·93	1·0	2·9
77	39	0·27	0·77	0·96	3·8
74	31	0·23	0·75	1·0	7·8
71	26	0·19	0·7	0·93	24·6
69·5	16	0·12	0·62	0·87	45·0
69	12	0·07	0·62	0·65	53·0

TABLE IV.

(*d*) 50% *Phenol.*

Temperature of the mixture °C.	ρ_h %	ρ_v %	ρ_u (observed) %	ρ_u (calculated) %	Relative intensity of the transversely scattered light
90	100	2·1	4·0	4·1	1·0 (assumed)
85	95	1·6	3·3	3·2	1·3
80	93	1·2	2·5	2·5	1·7
75	80	0·84	2·1	1·9	2·1
70	70	0·62	1·5	1·3	3·2
66·5	51	0·32	1·0	0·95	4·8
64·5	41	0·27	1·0	0·93	8·2

TABLE V. (*e*) 60% *Phenol.*

Temperature of the mixture °C.	ρ_h %	ρ_v %	ρ_u (observed) %	ρ_u (calculated) %	Relative intensity of the transversely scattered light
89	100	4·5	8·2	8·6	1·0 (assumed)
79	100	3·8	7·2	7·3	1·2
70	100	2·8	5·3	5·5	1·6
65	100	2·4	4·8	4·7	2·3
61	100	1·9	3·8	3·7	3·7

TABLE VI. (*f*) 70% *Phenol.*

Temperature of the mixture °C.	ρ_h %	ρ_v %	ρ_u (observed) %	ρ_u (calculated) %	Relative intensity of the transversely scattered light
59	100	9·3	16·3	17·0	1·0 (assumed)
49	100	8·2	14·9	15·1	1·2
40	100	6·9	12·2	12·9	1·3
30	100	6·0	11·0	11·3	1·5

TABLE VII.

Composition of the mixture *i.e.*, % by weight of Phenol	Temperature of miscibility °C.	ρ_h %	ρ_v %	ρ_u %	Relative intensity of opalescence
15	60	100	0·5	1·0	6·6
28	68·5	22	0·15	0·62	71
34	**69**	**12**	**0·07**	**0·62**	**186**
50	64·5	41	0·27	1·0	15
60	61	100	1·9	3·8	3
70	30	100	6·0	11·0	1 (assumed)

5. *Discussion of Results.*

In the tables given above the numbers given in the fifth column are the values of ρ_u calculated from the observed values of ρ_h and ρ_v using the reciprocity formula.[5] The observed values of ρ_u are in satisfactory agreement with the calculated values.

The experimental results show some very striking characteristics. For a mixture having any composition whatsoever, the values of the depolarisations ρ_u, ρ_v and ρ_h are minimum at the critical point, while the intensity of light scattered transversely is a maximum at this temperature. Again the depolarisations ρ_u, ρ_v and ρ_h attain minimum values and the intensity of scattering attains the maximum value for the mixture having the exact critical composition, *i.e.*, in this case for a mixture containing 34% by weight of phenol (see Table VII). The temperature of complete miscibility, as is well known, is also maximum for this concentration. As we go away from the critical composition on either side, the temperature of complete miscibility decreases, the depolarisation values increase suddenly at first and then gradually. In the same manner, the intensity of scattering falls off suddenly to less than half its value for the critical solution mixture, when the composition differs from the critical composition even by a small amount. For any mixture and especially for a critical composition mixture, there is a very rapid increase in the intensity of scattering as the critical solution temperature is approached. If curves are drawn showing (1) the dependence of depolarisation on composition, (2) the temperature of complete miscibility on composition, and (3) the intensity of scattering on composition, they will have approximately the same parabolic form.

It is seen from the results obtained that ρ_h for mixtures containing 15% by weight of phenol, 60% phenol and 70% phenol *has always the limiting value* of 100% showing thereby that no detectable clusters are present in these mixtures. In the case of the other three mixtures (*i.e.*, mixtures containing 28% phenol, 34% phenol and 50% phenol) detectable clusters are formed as is seen from the fall in the value of ρ_h from 100%. The range over which such clusters are detectable is less than 20° C. for mixtures containing 28% phenol and 50% phenol, while the range is more than 30° C. for a 34% phenol mixture. The values of ρ_h and ρ_v for the 34% phenol mixture at the critical solution temperature are considerably lower than the corresponding values for other mixtures. But the values of ρ_u is of the same order of magnitude. These definitely indicate that not only is the tendency for the formation of molecular clusters a maximum for the critical composition

[5] R. S. Krishnan, *Proc. Ind. Acad. Sci.*, 1935, **1A**, 782.

mixture, but also that the size of the clusters formed is greatest for this mixture. These results are in accordance with the remark made by H. S. Taylor[6] in his book on Physical Chemistry, that *it is only with the critical composition in a system containing two partially miscible liquids that a critical state can be reached.*

6. *Relation to Other Physical Properties.*

Various other physical properties such as viscosity, flow birefringence, magnetic birefringence, etc., have been extensively studied by numerous investigators. Ostwald and Malss[7] have determined the coefficient of viscosity for a series of binary mixtures of the type phenol and water both above and below the critical solution temperature. Only mixtures having the exact critical composition have been studied by them. They find an abnormal increase in the viscosity at the critical point. They try to explain the same by saying that liquid mixtures at the critical solution temperature are emulsoid systems of approximately colloidal degree of dispersion. Ostwald and Erbring[8] further found a marked streaming double refraction for a mixture of carbon disulphide and methyl alcohol within a definite region of temperature in the neighbourhood of the critical solution temperature.

A. Piekara[9] has investigated the variation of magnetic birefringence with temperature at different concentrations in mixtures of nitrobenzene and normal hexane. He finds that the thermal coefficient of magnetic birefringence increases with concentration, the coefficient becoming abnormally large at the critical solution point. The results are explained by him by assuming that the increase in the molecular association causes an increase in the molecular and magneto-optic anisotropy. These abnormal properties exhibited by critical composition mixtures near the critical point are in all probability due to the formation of molecular clusters under these conditions.

Critical composition mixtures near the critical point cannot be regarded as colloidal solutions or emulsoids since some important characteristics of a colloidal solution are not exhibited by these mixtures. A colloidal system progressively changes with time. But it is a fact of observation that the critical opalescence and such other phenomena exhibited by critical solution mixtures are invariant with time and depend only on the temperature. Moreover, if liquid mixtures at the point of complete miscibility behave like emulsoid systems, then all the phenomena which are characteristic of

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[6] H. S. Taylor, *A Treatise on Physical Chemistry*, Vol. **1**, 530.
[7] W. Ostwald and A. Malss, *Koll. Zeits.*, 1933, **63**, 61.
[8] W. Ostwald and Erbring, *Koll. Zeits.*, 1933, **64**, 229.
[9] A. Piekara, *Jour. de Phys.*, 1934, **5**, 54.

the critical composition mixture should also be exhibited by mixtures whose compositions are widely different from the critical composition. But this is not so. Although large molecular clusters are formed in binary liquid mixtures at the critical solution temperature, there seems to be no justification for regarding them as colloidal systems.

In conclusion, the author wishes to record his indebtedness to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his kind and helpful interest in the work.

7. *Summary.*

This paper deals with a comparative study of the intensity and depolarisation of the light scattered transversely by mixtures of phenol and water in different proportions and at different temperatures. The lowest values for the depolarisations ρ_u, ρ_v and ρ_h are obtained with the critical composition mixture (in this case 34% phenol mixture) at the critical solution temperature, where ρ_u, ρ_v and ρ_h are the depolarisations of the light scattered transversely when the incident light is (1) unpolarised, (2) polarised with electric vector vertical, and (3) polarised with electric vector horizontal respectively. The photoelectric method was employed for the comparison of intensities of scattering by these mixtures at various temperatures above the critical solution temperature. The intensity of scattering is found to increase considerably for the 34% phenol mixture as the critical solution temperature is approached. It is found that the tendency for the formation of clusters and the size of the clusters formed depend on the temperature and composition of the mixture. These phenomena are found to be most pronounced for the critical composition mixture at the critical solution temperature. The bearing of these results on the anomalies of viscosity, magnetic birefringence, etc., noticed in the vicinity of the critical conditions is also pointed out.

ON THE DIPOLE MOMENT OF TETRALIN.

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AND
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M. Puchalik[1] has recently reported that tetralin (tetrahydronaphthalene) exhibits in benzene solutions considerable association, and a dipole moment of value $1 \cdot 66 \times 10^{-18}$ e.s.u. Now, this value of moment is unusually high for a pure hydrocarbon. Experimental measurements have so far shown[2] that with the exception of the unsymmetrically substituted acetylene hydrocarbons, investigated by Otto and Wenzke,[3] almost the whole gamut of hydrocarbons of whatever shape and structure show moment values only between 0·5 to 0·0. Even here, the higher values are shown generally by unsymmetrically substituted ethylene compounds, and some benzene derivatives. More recently rather high values of moment have been reported by Svirbely, Albard and Warner[4] for *d*-pinene and *d*-limonene: these values, however, require confirmation, particularly as the measurements have been carried out at extremely dilute solutions where the experimental errors have enormous effect on the calculated values of moment.[5] It was, therefore, deemed necessary to check up the high value reported for the moment of tetralin and all the more so, as almost pure tetralin is available in commercial quantities and could be used as a solvent in dipole moment measurements.

Experimental.

The tetrahydronaphthalene used in these experiments was prepared from a "pure" stock, by drying over phosphorous pentoxide, and two successive slow fractional distillations in an all-glass apparatus under reduced pressure. The middle fraction boiling at a very steady temperature was collected for use: $d_4^{25°} = 0 \cdot 9639$, $n_D^{25°} = 1 \cdot 5382$.

The dielectric constant and density of the pure tetralin itself was measured initially, over the temperature range 10 to 40°, with the apparatus and methods described already.[6] The experimental values together with the

[1] M. Puchalik, *Acta. physic. Polon.*, 1933, **2**, 305–310. See *Sci. Abs.*, 1934, 1294.
[2] "Table of Dipole Moments, Class 2B," *Trans. Farad. Soc.*, 1934, **30**.
[3] M. M. Otto and H. H. Wenzke, *J. Amer. Chem. Soc.*, 1934, **56**, 1314.
[4] W. J. Svirbely, J. E. Albard and J. C. Warner, *Ibid.*, 1935, **57**, 652.
[5] M. A. Govinda Rau and B. N. Narayanaswamy, *Zeit. phys. Chem.*, (B), 1934, **26**, 25.
[6] M. A. Govinda Rau and B. N. Narayanaswamy, *loc. cit.*

calculated values for the molecular polarisations are presented in Table I. It is at once evident from the low value for the dielectric constant, and the very slight *decrease* in molecular polarisation with temperature, that tetralin is a nearly non-polar liquid, whose molecules have a finite but small moment. For, experimental measurements on all definitely non-polar liquids have hitherto shown a small but finite *rise* in molecular polarisation values with temperature,[7] a behaviour which is satisfactorily accounted for on the basis of the Raman-Krishnan theory of liquid structure.[8] If it is assumed that the Debye equation can be directly applied to the polarisation values for the pure liquid state,[9] the calculated value for the moment of tetralin comes out as $0{\cdot}41 \times 10^{-18}$.

TABLE I.

Pure Tetralin.

Temperature in °C.	Dielectric constant (E)	Density (d)	$P = \frac{E-1}{E+2} \cdot \frac{M}{d}$
10 ..	2·785	0·9760	50·51
20 ..	2·756	0·9679	50·42
30 ..	2·727	0·9599	50·30
40 ..	2·697	0·9519	50·16

The difficulties in determining to the usual degree of accuracy moments of this order of magnitude by the method of dilute solutions have been discussed frequently in the literature.[10] Thus, when the so-called "optical" method of calculating moment is employed, usually unsatisfactory results are obtained as there is no reliable method of determining the exact value of the induced or displacement polarisation. On the other hand when the method of temperature coefficient of molar polarisation is employed an increased accuracy, at least ten times in the dielectric constant and density values, is called for, or else the temperature range over which the molar polarisation is determined must be considerably enlarged. As in the present case benzene is

[7] C. P. Smyth and W. N. Stoops, *Jour. Amer. Chem. Soc.*, 1928, **50**, 1883; R. W. Dornte and C. P. Smyth, *Ibid.*, 1930, **52**, 3546; L. E. Sutton, R. G. A. New and J. B. Bentley, *Jour. Chem. Soc.*, 1933, 652; F. Fairbrother, *Proc. Roy. Soc.*, (A), 1933, **142**, 173; W. Lautsch, *Zeit. phys. Chem.*, (B), 1928, **1**, 115; H. Ulich, E. Hertel and W. Nespital, *Ibid.*, 1932, **17**, 369.

[8] C. V. Raman and K. S. Krishnan, *Proc. Roy. Soc.*, (A), 1927, **117**, 589; *Phil. Mag.*, 1928, **5**, 498; K. S. Krishnan, *Proc. Roy. Soc.*, (A), 1929, **126**, 155.

[9] L. M. Heil, *Phys. Rev.*, 1932, **39**, 666; J. Estermann, *Zeit. phys. Chem.*, (B), 1928, **1**, 134.

[10] See M. A. Govinda Rau and B. N. Narayanaswamy, *loc. cit.*

the solvent in which the high moment has to be examined, the temperature range over which measurements could be made stands limited. Further, as the methods and apparatus used to determine the dielectric constant and density were the same as before, it was hoped to obtain any improvement in accuracy by determining these values over a larger range of concentrations, particularly as with weakly polar solutes and non-polar solvents, the dielectric constant and density can be reasonably expected to be a linear function of concentration over a much larger range. This was realised in the present experiments. The slopes α and β of dielectric constant and density respectively with molar concentration were read off correct to 0·001 and 0·0001, and the $P_{2\infty}$ values calculated by the Hedestrand formula (Table II). The resulting slope of $P_{2\infty} - {}^{1}/_{T}$ calculated by the method of least squares gave a moment value of $0{\cdot}40 \times 10^{-18}$ e.s.u.

This moment was also calculated by the "optical" method as a further check. There are here usually two methods employed, the one in which the total induced polarisation is taken as the molar refractivity for the sodium D line, and the other in which it is taken as equal to $MR_{\infty}+15\%$ of same, where MR_{∞} is the extrapolated value of molar refractivity for infinite wave-length.

TABLE II.

(i)

Concentration in mol. fraction	10°		20°		30°		40°	
	E	d	E	d	E	d	E	d
0	2·303	0·8884	2·284	0·8777	2·265	0·8669	2·245	0·8561
0·01671	2·319	0·8908	2·300	0·8801	2·281	0·8694	2·263	0·8587
0·02750	2·329	0·8924	2·309	0·8818	2·289	0·8712	2·269	0·8606
0·03469	2·333	0·8930	2·314	0·8826	2·294	0·8723	2·274	0·8619
0·05204	2·350	0·8956	2·329	0·8852	2·309	0·8748	2·288	0·8644
0·06356	2·355	0·8970	2·334	0·8866	2·313	0·8763	2·292	0·8659
0·09105	2·378	0·9012	2·357	0·8909	2·337	0·8808	2·316	0·8706

The value of MR_D calculated from our data is 42·91 c.c.; and when subtracted from the value of $P_{2\infty}$ at 20°, gives an orientation polarisation of 9·51 c.c., corresponding to a moment of $0{\cdot}67 \times 10^{-18}$. On the other hand

(ii)

t°C.	α	β	$P_{2\infty}$
10 ..	0·820	0·1412	52·49
20 ..	0·803	0·1445	52·42
30 ..	0·789	0·1520	52·24
40 ..	0·781	0·1590	52·17

the value of MR_∞ calculated from the values of Auwers,[11] is 41·19, and the moment calculated by the second method $0{\cdot}49 \times 10^{-18}$. This value agrees better with those determined by the temperature coefficient methods. It is interesting that an exactly similar observation has been made in a recent paper by Briegleb and Kambeitz,[12] where it is found that a value of 1·15 MR_∞ for the induced polarisation leads to a more passable value for the moment of symmetrical trinitrobenzene.

Discussion.

To a rather rough approximation tetralin could be regarded as an alkyl ortho disubstituted benzene derivative, and the moment should therefore be of the order of that of ortho-xylene, *i.e.*, of about $0{\cdot}5 \times 10^{-18}$. This is just what has been observed for tetralin. The high value of moment reported by Puchalik is therefore improbable. A closer consideration of the structure of tetralin is at present difficult. While it is obvious that the two carbon atoms of the two CH_2 groups directly attached to the benzene ring must be in the plane of the ring, the other two carbon atoms in the remaining CH_2 groups can lie either in the plane of the other atoms or displaced from it. The structure of this saturated half of tetralin should be exactly analogous to that of cyclohexene (C_6H_{10}). A study of the moment of this compound should throw some light on the origin of the moment of tetralin, and the influence, if any, of the aromatic unsaturated half of tetralin on the aliphatic saturated half. Work on these lines is under progress.

Summary.

The moment of tetralin as measured in benzene as solvent is only 0·4 to $0{\cdot}5 \times 10^{-18}$, and not $1{\cdot}66 \times 10^{-18}$ as reported by Puchalik, The origin of this small but finite moment is briefly discussed.

[11] V. Auwers, *Berichte*, 1913, **46**, 2990, quoted by Landolt Tabellen.

[12] G. Briegleb and J. Kambeitz, *Zeit. phys. Chem.*, (B), 1934, **27**, 11. See also G. Briegleb, *Zeit. phys. Chem.*, (B), 1932, **16**, 276.

DOPPLER EFFECT IN LIGHT SCATTERING IN LIQUIDS.

Part II. Polarisation of the Transversely Scattered Radiations.

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

In previous communications, the author described experiments dealing with the examination of molecularly scattered light with the aid of a Fabry-Perot Interferometer and a specially-designed cathode-cooled low-density mercury vapour lamp.

In the first of these communications[1] which concerned itself with the study of the fine structure of the radiations scattered by liquid benzene in the backward direction, the author successfully demonstrated the reality of the two Doppler components appearing one on either side of the central undisplaced line. There was no indication, however, of the other components of higher frequency shifts reported by Gross.[2] The formula of Brillouin was also checked, the calculated values of the frequency shifts agreeing particularly well with the observed values for the mercury radiations, 4047 Å, 4078 Å and 4358 Å.

In the next paper[3] were reported some results concerning the relative intensities of the central undisplaced line to the outer Doppler components in the two liquids, carbon tetrachloride and toluene, chosen specially in view of the fact that the first liquid has optically isotropic molecules, while the latter has a relatively high degree of molecular anisotropy. The central undisplaced component appeared with great intensity in carbon tetrachloride, which indicates that the optical anisotropy of the molecules is not primarily responsible for the appearance of this central component. The Fabry-Perot pattern with toluene showed a strong continuous spectrum overlapping the triplet. This feature was almost entirely absent in the pattern obtained with carbon tetrachloride. From this it may be concluded that the continuous

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1 B. V. Raghavendra Rao, *Proc. Ind. Acad. Sci.*, 1934, **1**, 261.
2 E. Gross, *Nature*, 1930, **126**, 400.
3 B. V. Raghavendra Rao, *Proc. Ind. Acad. Sci.*, 1935, **1**, 473.

spectrum is a Raman effect due to the hindered rotation or angular oscillation of the molecules in the liquid, the intensity of this being naturally a function of the optical anisotropy of the molecules.

The third paper of the series[4] dealt with the influence of change of temperature of the liquid on the fine structure of the scattered radiation. On heating liquid carbon tetrachloride to 70° C., the Doppler components on either side of the central undisplaced component became fainter and broader, and tended to merge with the central line which brightened up in intensity. The Doppler components were also found to approach the central line with rise of temperature. These results suggest that the Brillouin theory of the Doppler effect departs from the truth, as the temperature of the liquid is raised.

The present paper describes a study of the state of polarisation of the three components observed in the spectrum of the scattered light when examined with a Fabry-Perot etalon. Beyond a casual statement by Gross[5] in one of his communications to *Nature*, very little work appears to have been done on this subject. Hence it was thought important to undertake a careful examination of this question. For this purpose, it is necessary to observe the light scattered in the transverse direction, though this direction is not so well suited for a separation of the Doppler components from the central line, owing to their closer approach to it.

2. *Experimental Arrangements.*

Since in this case we have to examine the transversely scattered light, a horizontal type of low-density cathode-cooled mercury vapour lamp has been designed as shown in Fig. 1. The intensity of this lamp is enhanced

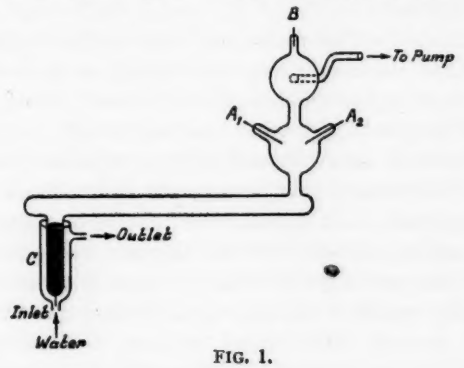

FIG. 1.

[4] B. V. Raghavendra Rao, *Proc. Ind. Acad. Sci.*, 1935, **1**, 765.
[5] E. Gross, *Nature*, 1930, **126**, 400.

by running two arcs simultaneously with the aid of the two anodes and the common mercury cathode. A parallel beam of light from this lamp is made to illuminate the side of the Wood's tube along its axis, by means of a big 8″ condenser. A large square-ended Nicol is placed between the observation window of the Wood's tube and the Fabry-Perot etalon, and the emerging interference pattern of the scattered light is focussed on to the slit of a Füess spectrograph by a lens. Two separate spectra are recorded in each case, one with the Nicol having its vibration axis vertical and the other with the vibration axis horizontal. Three liquids have been studied, namely, carbon tetrachloride, toluene and carbon disulphide, chosen as representative cases of molecules having respectively no optical anisotropy, moderate anisotropy and a high degree of anisotropy.

3. *Results.*

Carbon tetrachloride.—In the vertical position of the vibration axis of the Nicol, the interference pattern of the scattered light is characterised by the appearance of the central line and the two Doppler components on a very clear background. In the horizontal position of the Nicol, nothing was recorded on the plate, in spite of extended exposures of the order of 48 hours. The results indicate that all the three components are completely polarised, and that a continuous spectrum if it is present is extremely weak.

Toluene.—In the vertical position of the vibration axis of the Nicol, all the three components are present and can be observed in the interference pattern of the scattered light superimposed on a continuous background. In the horizontal position of the Nicol, only the continuous background is recorded in the spectrum, and no trace of the three components could be detected with certainty.

Carbon disulphide.—The results are very similar to those in the case of toluene except that the continuous spectrum is somewhat stronger. Exposures ranging from a few hours to 48 hours were given with the vibration axis of the Nicol horizontal, to see if the presence of any of the three components could be detected superimposed on the continuous background. There were very faint indications of the presence of Fabry-Perot rings crossing the continuous background, and it was uncertain as to whether they belonged to the central undisplaced line or the Doppler components. It may be mentioned here that any experimental defects such as the angle of scattering being indefinite by reason of the use of a source of finite length, as also the presence of any parasitic light, ought to have, if anything, given a central undisplaced line in the horizontal component of the scattered light.

The plate reproduces the interference patterns of the three liquids as negatives for clearness of reproduction.

4. *Significance of the Results.*

So far as the two Doppler components are concerned, we should expect them to be completely polarised, as is indicated by the observations, since they arise from density fluctuations due to the presence of sound waves of various wave-lengths associated with the thermal energy of the medium. The further result indicated by observation, namely, that the central undisplaced component is also completely polarised seems at first sight very surprising, especially when we remember that the polarisation of transversely scattered light is very imperfect to the extent of 46% in toluene and 62% in the case of carbon disulphide. We know however that the central undisplaced line appears with great intensity also in the case of carbon tetrachloride, and its appearance is therefore not primarily ascribable to the optical anisotropy of the molecule. This makes it easier to understand why it should be more or less completely polarised. We may assume that the undisplaced line is due to the scattering of light by individual molecules or by groups of molecules in the liquid which are free to rotate or oscillate. The Q branch in the spectrum of the scattered light due to such molecules or groups of molecules should be more or less completely polarised. For instance, in the case of carbon disulphide, the total scattering by individual molecules would show a defect of polarisation only to the extent of 11% and if we consider only the Q branch the defect would be only a fraction of this, of the order of a few per cent. The Q branch in the scattering by groups of molecules, unless they are highly unsymmetrical in shape, should be even more completely polarised.

These observations and the foregoing remarks make it clear why in the horizontal component of the scattering by liquids, the Q branch, if present at all, is extremely weak. Further, it follows that practically the whole of the depolarisation of the light scattered by liquids at ordinary temperatures is to be ascribed to the presence of a continuous spectrum of radiation of altered wave-length. The presence of such continuous radiation in the light scattered by liquids and its marked imperfection of polarisation were discovered simultaneously with the presence of sharp lines of altered wave-lengths.[6] The spectral character of this radiation, namely, that of a nebulosity or wings accompanying the primary and the displaced lines in the spectrum of the scattered light is shown by the very earliest photographs and microphotometer records of Raman spectra.[7] The fact that this continuous

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[6] C. V. Raman, *Ind. Jour. Phys.*, 1928, **2**, 395 ; *Nature*, 1928, **121**, 619.

[7] C. V. Raman, *Nature*, 1928, **121**, 711.
C. V. Raman and K. S. Krishnan, *Ind. Jour. Phys.*, 1928, **2**, Plate 13, Fig. 6 and Plate 16.

spectrum is almost completely unpolarised, that its intensity increases with the optical anisotropy of the molecule and that it is unsymmetrical about the lines which it accompanies, led Raman and Krishnan[8] to suggest that it arises from the impeded rotations of the molecules in a dense fluid. Though much has been written on the subject, this original explanation still holds the field if we add the qualification that the impeded rotation may take the form of approximately periodic angular oscillations of the molecule and that account is also taken of the impeded rotation or oscillation of groups of molecules.[9]

In view of what has been said above, it is difficult to attach much significance to the measurements which have been published of the depolarisation of light scattering in liquids made spectroscopically with slits of varying width. Mr. S. Venkateswaran[10] who made a series of measurements of this kind showed that the depolarisation of light scattering diminishes as the slit width employed is narrowed. He also remarked that this diminution is much less conspicuous for highly associated liquids such as acetic acid, formic acid,...,etc., than for non-associated liquids, *e.g.*, benzene and carbon disulphide. Rousset[11] who has pursued the subject further has shown that by using still finer slits, values for the depolarisation lower than those reported by Venkateswaran may be obtained. If we are to credit the results obtained in the present paper with the Fabry-Perot etalon, the depolarisation thus measured is simply a function of the resolving power of the instrument, and still lower values should be obtained by using spectrographs of great power and the finest slits possible. This is a subject which appears well-worth pursuing, in order to confirm the provisional conclusion that the Q branch is practically absent in the horizontal component of the scattering by liquids, and to ascertain the size of the molecular groups present and responsible for the continuous spectrum given by the various types of liquids. It appears desirable also to extend the work with the Fabry-Perot etalon using highly associated liquids such as formic and acetic acids, and also to re-examine the case of non-associated liquids using fine slits and an auxiliary spectrograph of greater power as to eliminate the obliterating effect of the superimposed continuous spectrum. Quantitative estimates of the imperfection of polarisation of the central undisplaced component would evidently be desirable in all these cases. Work on these lines is in progress.

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[8] C. V. Raman and K. S. Krishnan, *Nature*, 1928, **122**, 278 and 882; *Proc. Roy. Soc.*, 1929, **122**, 30.

[9] S. Bhagavantam, *Proc. Ind. Acad. Sci.*, 1935, **2**, 63.

[10] S. Venkateswaran, *Phil. Mag.*, 1932, **14**, 258.

[11] Rousset, *C. R.*, 1933, **197**, 1033.

Carbon tetrachloride

(*a*)

Toluene

(*b*)

Carbon disulphide

(*c*)

In conclusion the author desires to express his grateful thanks to his professor Sir C. V. Raman, for his kind interest and helpful guidance during the progress of this work.

Summary.

The present paper describes a study of the state of polarisation of the three components observed in the spectrum of the scattered light when examined with a Fabry-Perot etalon. Three typical liquids, carbon tetrachloride, toluene and carbon disulphide have been examined. The results indicate that the two Doppler components are completely polarised as is to be expected, and that the central component is practically completely polarised. The significance of the latter result which appears surprising at first sight, is discussed in some detail.

A THEOREM ON THE ADDITION OF RESIDUE CLASSES: APPLICATION TO THE NUMBER $\Gamma(k)$ IN WARING'S PROBLEM.

By Inder Chowla.

Received August 9, 1935.
(Communicated by Dr. S. Chowla.)

1. Davenport[1] has recently proved the following remarkable Theorem:

Let p *be a prime; let* $\alpha_1, \cdots, \alpha_m$ *be* m *different residue classes* (mod p); *let* $\beta_1, \cdots, \beta_n$ *be* n *different residue classes* (mod p). *Let* $\gamma_1, \cdots, \gamma_l$ *be all those different residue classes which are representable as*

$$\alpha_i + \beta_j \quad (1 \leqslant i \leqslant m, \ 1 \leqslant j \leqslant n).$$

Then $l \geqslant m+n-1$ *provided* $m+n-1 \leqslant p$, *and otherwise* $l=p$.

In this paper we generalize this theorem to any composite modulus. We can only do this by introducing certain restrictions on one of the sequences. In fact it is easy to show by an example that the theorem is not, as it stands, true for non-prime moduli.

Example. Let the modulus be 81, and let the α's be the positive integers $\equiv 1(9)$ and less than 81, so that $m=9$; let the β's be the positive integers $\equiv 2(9)$ and less than 81, so that $n=9$. Then it is easy to see that the γ's are the positive integers $\equiv 3(9)$ and less than 81, so that $l=9$. Hence $l=m+n-9$ so that the theorem is not true.

Our theorem, which is not a complete generalization, is as follows:

Theorem 1. Let k *be a positive integer; let* $\alpha_1, \cdots, \alpha_m$ *be* m *different residue classes* (mod k); *let* $\beta_1, \cdots, \beta_n$ *be* n *different residue classes* (mod k) *where one of the* β's *is* 0 *and the rest are prime to* k. *Let* $\gamma_1, \cdots, \gamma_l$ *be all the different residue classes which are representable as*

$$\alpha_i + \beta_j \quad (1 \leqslant i \leqslant m, \ 1 \leqslant j \leqslant n).$$

Then $l \geqslant m+n-1$ *if* $m+n-1 \leqslant k$, *and otherwise* $l=k$.

That the number $m+n-1$ in this theorem cannot be replaced by a greater number is shown by the following

Example. Let the α's be the positive integers $\equiv 1(9)$ and less than 81; let the β's be the number 0 and the positive integers $\equiv 2(9)$ and less tha

[1] *Journ. London Math. Soc.*, 1935, **10**, 30-32.

81. Then $m=9$, $n=10$. The γ sequence consists of the positive integers $\equiv 1(9)$ and $\equiv 3(9)$ and less than 81. Hence $l=18$, and $l=m+n-1$.

2. This theorem has applications to the number $\Gamma(k)$ in Waring's problem. Let us define $\Gamma(k)$ as the least s such that every arithmetical progression contains an infinity of numbers of the form $x_1^k + \cdots + x_s^k$ where the x's are integers. Hardy and Littlewood[2] have proved that $\Gamma(k) \leqslant 4k$, while $\Gamma(k)=4k$ for infinitely many k. It is an easy consequence of theorem 1 that

Theorem 2. Let $s \geqslant 4k$, *and let the integers* a_r $(r \leqslant s)$ *be prime to* a. *Then, every arithmetical progression* $ax+m$ *contains infinitely many numbers of the form*

$$a_1 x_1^k + \cdots + a_s x_s^k$$

where the x's *are integers.*

The particular case $a_1 = \cdots = a_s = 1$ gives $\Gamma(k) \leqslant 4k$. Detailed proofs will appear elsewhere.

[2] "Some Problems of 'Partitio Numerorum': IV," *Math. Ztschr.*, 1922, **12**, 161-188 (Theorem 12, page 186).

MAGNETIC DOUBLE REFRACTION AND LIGHT SCATTERING IN FUSED NITRATES.

By V. N. Thatte,
Department of Physics, College of Science, Nagpur.

Received August 20, 1935.

(Communicated by Prof. K. S. Krishnan.)

The paper gives an account of measurements on the light scattering and magnetic double refraction of some fused nitrates. The magnetic and optical anisotropies of the NO_3 group are calculated therefrom, and are found to be the same as for the NO_3 group, in nitric acid and in crystalline nitrates.

1. *Introduction.*

In a recent investigation on the Raman spectra of fused inorganic nitrates[1] it was observed that the Raman lines characteristic of the nitrate ion appear in practically the same positions as in the spectra of aqueous solutions of the nitrates, suggesting that the structure of the ion is the same in both the states. In order to find whether other physical properties of the ion, as for example its magnetic and optical anisotropies, are also the same in fused nitrates as for the free ion in aqueous solution, we have made some experimental studies on light scattering and magnetic double refraction of fused nitrates. The present paper gives a report on these studies. Fused zinc and cadmium nitrates were chosen for these studies, since they could be easily maintained in super-cooled condition over a wide range of temperatures.

2. *Light Scattering.*

(i) *Polarisation of the scattered light.*—The depolarisation factor of the scattered light from the fused nitrates was measured by the usual method of Cornu with a double image prism and a nicol. It is not necessary to give here the experimental details since they are so well known. The following table gives the values of the ratio, r, of the weak component to the strong one in the transversely scattered light, when the incident light is unpolarised. The values of the depolarisation factor of scattered light from nitric acid of different concentrations are given below for comparison.

(ii) *Intensity of the scattered light.*—The intensity of the light scattering of the fused nitrates was measured by comparing it with the scattering by benzene at room temperature. This liquid was chosen for the comparison

[1] Thatte and Ganesan, *Ind. Jour. Phys.*, 1934, **8**, 341.
[2] S. Venkateswaran, *Ind. Jour. Phys.*, 1926, **1**, 235.

TABLE I.

Temp. °C.	Depolarisation factor, r	
	Zinc nitrate	Cadmium nitrate
30	·51	·44
46	·50	·43
65	·48	·41
84	·45	..
128	·36	·33
140	·31	·30

Strength of acid %	14·1	28·0	39·2	46·0	64·7
r	·36	·41	·48	·57	·64

since its absolute scattering has been measured accurately by Cabannes and others.

The experimental method adopted was as follows: A strong narrow beam of parallel light was allowed to pass through a cell with plane glass windows, containing dust-free benzene. The transmitted beam was then allowed to pass through a similar vessel containing the fused nitrate. The tracks of light in the two liquids were of nearly the same cross-section, and their intensities were compared with the help of an Abney rotating sector. The cell containing the fused nitrate was then replaced by a similar cell containing dust-free benzene, and again the intensity was compared with that of the benzene in the first cell. From these two measurements the intensity of the light scattering by the fused nitrates relative to that of benzene is known. (This method naturally eliminates the effects of any deviation from parallelism of the incident light.)

The measured intensities were as below. Taking the transverse scattering by benzene at 30° C. as unity, the scattering of fused zinc nitrate at 65° C. was 1·18, and that of fused cadmium nitrate at 70° C. was 1·40.

3. *Magnetic Double Refraction.*

The fused nitrate was kept in a double-walled tube, and was heated by a steady stream of hot water from a thermostat, circulating between the two walls; the temperature was maintained constant to within a degree.

The magnetic double refraction was measured by the arrangement described in detail by Chinchalkar in a recent publication.[3] The double refraction was compared with that of pure acetone, with the help of a Rayleigh strained glass compensator.

The experimental results are given in the following table. C_m denotes the double refraction, defined as usual by the expression

$$C_m = \frac{n_{\parallel} - n_{\perp}}{\lambda H^2} \qquad .. \qquad .. \qquad .. \qquad .. \qquad (1)$$

The second column in the table gives the values of C_m measured relatively to that of acetone, and the third column gives the absolute values calculated on the assumption that for acetone

$C_m = \cdot 016$ times that of nitrobenzene

$= \cdot 4 \times 10^{-13}$, for $\lambda = 589\ m\mu$.

Zinc nitrate ..	1·4	$5{\cdot}6 \times 10^{-14}$
Cadmium nitrate ..	1·25	$5{\cdot}0 \times 10^{-14}$

4. *The Optical Anisotropy of the* NO_3 *ion.*

From the scattering data given in the previous section, the optical anisotropy of the NO_3 group can be calculated. In the first place it is known from X-ray measurements on the crystalline nitrates that the NO_3 group has a plane structure, with the three O atoms at the corners of an equilateral triangle and the N atom at the centre. With such a structure the two optical polarisabilities of NO_3 group in its plane should be equal and much greater than that along the normal to the plane. Let A = B and C be respectively the three polarisabilities. Let us assume that in the fused state the nitrate is more or less completely ionised, *i.e.*, that the metallic ions, *viz.*, Zn^{++} or Cd^{++} are not permanently attached to NO'_3. Since these metallic ions are isotropic, the depolarisation of the scattering will be determined practically by the optical anisotropy of the NO_3 group, the metallic ions influencing it only indirectly through their contribution to the refractive index, and to the compressibility of the medium.

[3] *Ind. Jour. Phys.*, 1932, **7**, 491.

Defining as usual the optical anisotropy δ of the NO'_3 ion by the equation

$$\delta = \left(\frac{A-C}{2A+C}\right)^2 \quad .. \quad .. \quad .. \quad .. \quad (2)$$

the calculation of the anisotropy is easily made, since the necessary expressions have been derived by the earlier workers. We have

$$r = \frac{6\delta}{5kT\beta\nu + 7\delta} \quad .. \quad .. \quad .. \quad .. \quad (3)$$

where ν is the number of NO'_3 ions per c.c., k is the Boltzmann constant, T is the absolute temperature, and β is the compressibility. All the quantities in the above expression are known, except β, which can, however, be obtained indirectly from the intensity of the scattered light.

Calculating in this manner we find

$\beta = 101 \times 10^{-6}$ per atm. for zinc nitrate

and 121×10^{-6} per atm. for cadmium nitrate.

Substituting the values of the various quantities in (2), we obtain

$\delta = \cdot 038$ for the ions in zinc nitrate

and $\cdot 036$ for the ions in cadmium nitrate,

from which we obtain

$$\frac{A}{C} = 1 \cdot 9.$$

Thus the optical polarisability along directions in the plane of the NO_3 group is about twice that along the normal to the plane.

5. Comparison with Values of the Anisotropy obtained from Other Data.

The above value for the ratio $\frac{A}{C}$ agrees well with the value $\frac{A}{C} = 2 \cdot 0$ obtained from the depolarisation of light scattering by nitric acids of different concentrations.[4]

It is also possible, following the method of Bragg,[5] to calculate the anisotropy of the NO'_3 ion from the birefringence of crystalline sodium nitrate, in which the NO'_3 ions are all oriented parallel to one another and perpendicular to the trigonal axis. The ratio of the refractivity of the NO_3 ions in the crystal for light vibrations normal to the trigonal axis to that for vibrations along the axis is found to be $1 \cdot 67$. In order to obtain $\frac{A}{C}$ for the *free* NO_3 ion from the above ratio, we have to correct for the influence

[4] Krishnan and Raman, *Proc. Roy. Soc.* (A), 1927, **115**, 549.

[5] W. L. Bragg, *Proc. Roy. Soc.* (A), 1924, **106**, 346.

of the surrounding sodium and NO'_3 ions in the crystal. Making this correction we obtain

$$\frac{A}{C}=1\cdot8$$

which is nearly the same as the value obtained in the previous section.

6. Magnetic Anisotropy of the NO_3 *ion.*

The Cotton-Mouton constant C_m is given by the expression

$$C_m=\frac{(n^2-1)(n^2+2)(A'-C')\sqrt{\delta}}{30\,n\lambda\,kT} \qquad .. \quad .. \quad .. \quad (4)$$

Since the value of the optical anisotropy of the NO_3 group is now known, the above relation can be utilized to calculate the magnetic anisotropy of the ion, *viz.*, $(A'-C')$ from the known value of the Cotton-Mouton constant. We thus obtain

$A'-C'=4\cdot4\times10^{-6}$ per gram ion for zinc nitrate

and $4\cdot0\times10^{-6}$ per gram ion for cadmium nitrate.

These values are of the same order as that obtained by Krishnan and Raman from the magnetic double refraction of nitric acid, *viz.*, $5\cdot3\times10^{-6}$ per gram ion for nitric acid.

In sodium and potassium nitrates it is well known from X-ray data that the NO_3 groups are arranged in parallel planes so that the difference between the principal susceptibilities of the crystals for directions in the plane of the NO_3 group and along the normal to their planes should be equal to $A'-C'$. The magnetic anisotropy[6] for these crystals is equal to $4\cdot9\times10^{-6}$ per gram ion.

Thus we find that both the optical and the magnetic anisotropies of the NO_3' ion in fused crystals are practically the same as for these ions in other states, *viz.*, in state of solution and in crystals.

The author wishes to record his heart-felt thanks to Prof. K. S. Krishnan for his advice and keen interest in the work.

[6] Krishnan, Guha and Banerjee, *Phil. Trans.* (A), 1933, **231**, 235.

DIAMAGNETISM OF COPPER.

By Dr. S. Ramachandra Rao,
Annamalai University.

Received August 20, 1935.

1. *Introduction.*

In a recent paper,[1] the author has reviewed at some length the present position of our knowledge regarding the magnetic properties of colloidal particles of metals. A few general conclusions emerge from our perusal of the literature on this subject. Substances like graphite (which is not a metal) and bismuth (which is not a metal in the true sense of the term) show a decrease in the diamagnetic susceptibility value on colloidalisation. The elegant experiments of Krishnan and Ganguli[2] with blue graphite not merely confirm the effect in the case of graphite but also indicate definitely that the direction of largest decrease of susceptibility on colloidalisation is the one parallel to the hexagonal axis. To explain the high diamagnetism of these elements, it was suggested by Ehrenfest[3] and Raman[4] that some of the valency electrons had large orbits. Such orbits could not be possible on the surface and hence increase of surface area by colloidalisation would bring about a decrease in the specific diamagnetic susceptibility. This explanation obviously implies that the particles are much less densely packed on the surface than in the interior. The effect therefore of a smaller density of distribution on the surface is to decrease the effective specific diamagnetic susceptibility of the specimen and in the case of colloidal particles, the surface area is sufficiently large to decrease effectively the mean value of the diamagnetic susceptibility of the powder.

In the case of good conductors like copper, conditions are quite different. The valency electrons are considered here as free, the number of such electrons being of the same order as the number of atoms in the metal. Honda and Shimizu[5] have considered this question at some length and have quantitatively accounted for the increase of diamagnetism on cold-working.

Due to the expansion on cold-working, there is a diminution of free electrons and hence a decrease in the paramagnetic component due to them. According to Pauli,[6] this decrease $\delta\chi_1$ is given by

$$\delta\chi_1 = \frac{2}{3}\frac{C.L^{1/3}}{W^{1/3}}\left(-\frac{2}{3}\rho^{-5/3}\alpha^{1/3}\delta\rho + \frac{1}{3}\alpha^{-2/3}\rho^{-2/3}\delta\alpha\right) \quad .. \quad (1)$$

where $C = 2{\cdot}21 \times 10^{-14}$, L=the Loschmidt number, W=the atomic weight, ρ=the density, and α=the number of free electrons per atom.

At the same time there should be an increase in the diamagnetic component due to the increase in the number of bound electrons, since on expansion some of the otherwise free electrons get associated with atoms. Sommerfeld[7] has determined this increase $\delta\chi_2$ as

$$\delta\chi_2 = \frac{3{\cdot}1\times1{\cdot}84\times10^{-5}}{W} \cdot \frac{1}{3}a^{-2/3}\,\delta a \qquad .. \qquad .. \quad (2)$$

where $\delta a = \frac{A}{3}\left(\frac{4\pi\rho}{3M}\right)^{0{\cdot}488}\frac{\delta\rho}{\rho}$

in which $A = 2{\cdot}261\times10^{-12}\,Z^{0{\cdot}513}$ and M = mass of the atom, as calculated by Honda, Nishina and Hirone.[8] The total change in the susceptibility is given by $\delta\chi = \delta\chi_1 + \delta\chi_2$.

The net effect of cold-working is consequently to increase the diamagnetic susceptibility and this is exactly the result of the observations of Honda and Shimizu.

They have more recently[9] drawn attention to the close relations between colloidalisation and cold-working in metals. They explain that in the case of tin, the lattice constant is a little larger in the surface layer than in the interior, the normal value for the metal being reached at some hunderd layers below the surface. Thus colloidalisation should bring about increased diamagnetism quite similar to what is obtained in the case of cold-working. This was exactly the observation made by the writer.

The obvious interest aroused by this investigation led the author to undertake an inquiry into the behaviour of copper. Copper is of particular interest since it is a typical metal being a good conductor of electricity. Honda and Shimizu have investigated the effect of cold-working on this element and shown that there is an increased diamagnetism if the necessary corrections are made for the presence of ferromagnetic impurities. Copper crystallises in the cubic system with a face-centred structure, the side of the elementary cube being 3·597 A.U.[10] Any directional variations are thus out of question.

2. *Experiment.*

(*a*) *Purity of the specimen.*—The specimens of copper used were in the form of rods 5 mm. diameter, obtained from Adam Hilger. They were the purest available and had been subjected to a thorough chemical and spectroscopic examination. Hilger's report gave the following impurities in the specimen.

Iron	..	..	0·0041%
Nickel	..	..	0·0004%
Tin ..	..	..	0·0005%
Lead	..	..	0·0004%
Bismuth	..	..	Trace.

Thallium	..	Trace.
Calcium	..	0·0005%
Magnesium	..	0·0001%
Zinc	..	Trace.
Oxygen	..	0·030%
Total Impurities	..	0·036%

The amount of copper present in the specimen was thus 99·964% which should be regarded as more than sufficient for our purposes. The question of the presence of ferromagnetic impurities will be considered later.

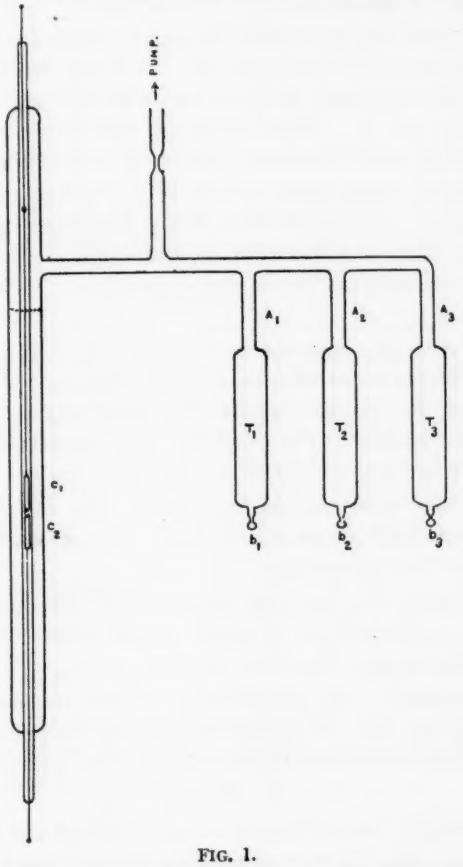

FIG. 1.

(*b*) *Preparation of the colloidal powders.*—The apparatus[11] used for colloidalisation is shown in Fig. 1. Two lengths of copper c_1 and c_2 were

cut to be about 2 cms. each and attached to two stout copper leads, such that the free ends faced each other. A gap of about 1 mm. was left as the sparking distance between the ends. After thoroughly cleaning the tube, pumping out, warming and drying, the sparking tube was filled with normal propyl alcohol or benzene. The tube was connected once again to the pump and after bringing down the pressure to the lowest obtainable, sparking was allowed to take place by connecting the leads to the secondary of an induction coil. The sparking currents were kept low, 2 to 8 milliamperes to minimize the heat produced; and the time of sparking ranged from $\frac{1}{2}$ to about $1\frac{1}{2}$ hours.

The coarser particles were then allowed to settle for about an hour and the pump connection was now sealed off. The clear liquid was then allowed to flow in T_1 till it was nearly full and the tube was next sealed off at the constriction drawn at A_1. Thus the liquid was allowed to fill successively the tubes T_2 and T_3, each tube being sealed off after filling.

The particles in these tubes were next allowed to settle by gravitation or were centrifuged. They were then filed a bit at the top and were broken open in vacuum. The liquid was drained off and by placing the entire tube in a heater, the remaining liquid was evaporated. The small bulbs were then sealed off.

After observing the magnetic deflections, the bulbs were broken open and the size of the particles determined with a high power microscope having an eye-piece scale which was calibrated by observing the lines of a diffraction transmission grating. The particles were mixed with a little propyl alcohol as otherwise they appeared in clusters in the field of view.

The glass bulbs were cleaned thoroughly with warm dilute nitric acid and then with hot distilled water and dried. The magnetic deflections were next observed for the bulbs alone.

In all cases the bulbs were weighed before and after removing the copper particles. The masses of the powders varied from about 10 to 40 mg., the error in weighing being less than 0·1 mg.

(*c*) *Measurements of the susceptibility.*—The Curie method was adopted to determine the specific susceptibilities of powders. Full details of this method and the calculation of results are given in an earlier paper.[12]

3. Results.

(*a*) *Mass metal.*—Small chips of copper were cut and pickled thoroughly with hydrochloric acid. They were then washed and dried. Several samples were investigated and the results for a few specimens at infinite field strengths are given below.

TABLE I.

Sample No.	Mass in grams	Diamagnetic susceptibility χ
1	0·2235	0·0805
2	0·1872	0·0803
3	0·2478	0·0798
4	0·1690	0·0800
5	0·2020	0·0799
6	0·1993	0·0797
7	0·2101	0·0798

The results give for copper in bulk a mean specific diamagnetic susceptibility of 0·080. This value compares favourably with those of other investigators given below.

TABLE II.

Investigator	Diamagnetic susceptibility χ
M. Owen[13]	0·085
K. Honda[14]	0·086
St. Meyer[15]	0·071
Koenigsberger[16] ..	0·088
Honda and Shimizu[17] ..	0·0848
Author[18]	0·080

The susceptibility of the specimens was determined at different field strengths. According to Honda,[19]

$$\chi_i = \chi_p + \frac{\sigma m}{H}.$$

where χ_p is the specific susceptibility of the pure sample, χ_i the corresponding value for the impure specimen and σ and m the specific intensity of magnetisation and mass of the ferromagnetic impurity present in unit mass of the

specimen. A graph drawn between χ_i and $\frac{1}{H}$ gives a straight line which could be extrapolated and the susceptibility determined for $\frac{1}{H} = 0$ or $H = \infty$. In this manner the disturbing effect of the ferromagnetic impurity can be eliminated.

In Fig. 2 are plotted the results obtained for four specimens. The diamagnetic susceptibility in all the cases works to a value in the immediate neighbourhood of 0·080.

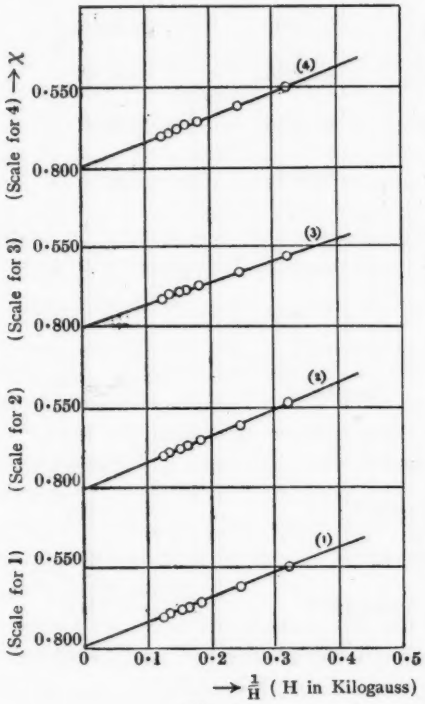

FIG. 2.

(*b*) *Colloidal particles.*—The results obtained for a dozen samples are tabulated below. For each sample, measurements were made at different field strengths and the value at infinite field strengths was obtained by extrapolating the χ, $\frac{1}{H}$ graph. The diameters of the particles in any sample were the same to within 5%. Fig. 3 shows the graph between the diameter of the particles and the susceptibility.

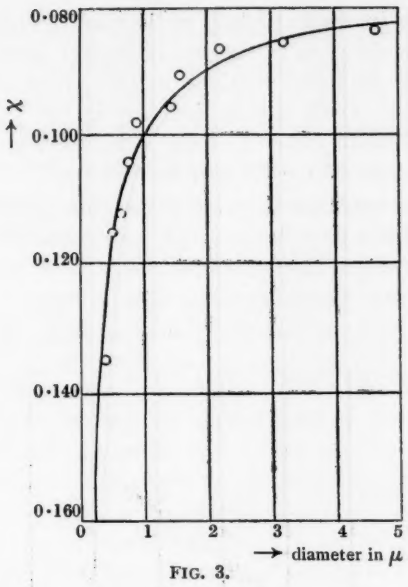

FIG. 3.

TABLE III.

Diameter of the particles	Mass in mg.	Dispersing medium	χ
10·0	38·8	*b*	0·083
6·0	40·2	*b*	0·083
3·2	32·1	*p*	0·085
2·2	23·7	*b*	0·086
1·6	26·3	*p*	0·090
1·5	27·2	*b*	0·095
1·0	30·2	*b*	0·094
0·9	18·6	*p*	0·098
0·75	17·7	*p*	0·100
0·65	21·3	*b*	0·112
0·5	17·4	*p*	0·115
0·4	19·5	*b*	0·135

b—Benzene; *p*—Propyl alcohol.

The susceptibility increases slightly as the particle diameter decreases to $0 \cdot 8\,\mu$. The value increases more rapidly at smaller particle sizes attaining $0 \cdot 135$ at the smallest diameter obtained in this investigation, $0 \cdot 4\,\mu$. The critical diameter below which a large increase in the susceptibility occurs is $0 \cdot 8\,\mu$. This is much smaller than the corresponding values for bismuth[20] ($1 \cdot 4\,\mu$), graphite[20] ($1 \cdot 5\,\mu$) and tin[21] ($2 \cdot 0\,\mu$).

It will also be noticed that the diamagnetic susceptibility depends only on the dimensions of the particles and not on the nature of the dispersing medium—benzene or propyl alcohol.

Fig. 4 shows the χ, $\frac{1}{H}$ curves for a few of the powders indicated. A point of great importance emerges from a scrutiny of the graphs. The

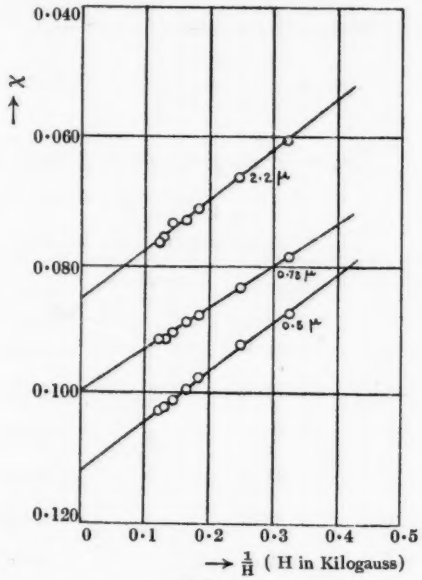

FIG. 4.

slopes of the straight lines are nearly the same, indicating that the ferromagnetic impurity occurs in the same state in all the powders investigated or that colloidalisation is not accompanied by any separation of the iron content causing spurious effects to enter into the magnetic measurements.

(*c*) *Heating the powders.*—A full description of the heating arrangement has been given in an earlier paper. Bits of copper and a few of the colloidal samples were heated and at each temperature for any specimen, the susceptibility at different field strengths was determined. It was found that the

diamagnetic susceptibility extrapolated to infinite field strengths was the same for any specimen at temperatures ranging from 30° C. to 350° C. Heating did not also change the slope of the χ, $\frac{1}{H}$ curves, indicating that the nature of the iron content was the same at all temperatures investigated.

4. Discussion.

We shall first consider the possibility of impurities giving rise to increased diamagnetism on colloidalisation. A reference[22] to the values of the susceptibilities of copper compounds indicates that the ordinary compounds of copper are either feebly paramagnetic or less diamagnetic than the metal. Further it has already been pointed out that the susceptibility of the colloidal powders depends only on the dimensions of the particles and not on the nature of the liquid in which colloidalisation is effected. It is thus most probable that the increase of diamagnetism with decreasing particle size is a genuine effect. This observation receives confirmation from the experiments of Honda and Shimizu on the effect of cold-working on the susceptibility of copper.

It was mentioned in section 1 that these authors observed a small increase of diamagnetism when copper was subjected to cold-working. The specific diamagnetic susceptibility changed from 0·848 to 0·926 (an increase of 0·078) as the density of the metal diminished from 8·9521 to 8·6646. On the basis of equations (1), (2) and (3), the calculated value of $\delta\chi$ for this change of density works to 0·064, which agrees very well with the observed value.

Honda and Shimizu have suggested that in the case of colloidal powders, the lattice constant is a little greater in the surface layer than in the interior, the normal value for the metal being reached at some hundred layers below the surface. Thus colloidalisation should be accompanied by increased diamagnetism quite similar to what is obtained in the case of cold-working. This is in accord with experiment.

The results with colloidal powders do not seem to lend themselves to a straight calculation of the susceptibility of the surface layer and its thickness. However by trial, it was found that the results fitted closely with the calculated values assuming the thickness of the surface layer to be 0·03 μ and its diamagnetic susceptibility 0·200. In fact in Fig. 3, the continuous line has been drawn to give the results calculated on the basis of these assumptions and it is found that the points plot themselves near the line.

The surface layer thus seems to be about 300 A.U. thick and hence contains nearly 80 atomic layers.

It follows from (1), (2) and (3) that

$$\delta\chi = K\,\delta\rho$$

where K is a constant for any given metal, *i.e.*, that the change in the susceptibility is directly proportional to the change in density. On calculation, it is found that $K = 0 \cdot 2226 \times 10^{-6}$ for copper. If the surface layer has a specific diamagnetic susceptibility of 0·200, then $\delta\chi = 0 \cdot 120$ which gives for $\delta\rho$ a value of 0·539. Since the density of the mass copper was found to be 8·943, that of the surface layer should be 8·404. It would be of interest to check this result by direct experiment but no density measurements seem to have been obtained so far with colloidal powders.

There is however one experimental fact which lends support to the view that the density of the superficial layer is less than the density of the mass metal. It is obvious that the lattice constant should be larger at the surface than in the interior. To investigate the surface layers, the recent electron diffraction experiments have come in very handy. G. P. Thomson[23] studied the surfaces of metallic single crystals by the electron reflection method. In these experiments only a few atomic layers are concerned. He deposited copper electrolytically on the etched surface of a copper crystal and discovered by electron diffraction methods that the spacing of part at least of the deposit was larger than that of normal copper, though the structure was roughly similar. The deposit was probably in the form of very minute crystals on the copper base and these gave rise to the new spacing presumably because of their smaller density. In fact the spacing in certain cases was found to be 4·5 A.U. while that of ordinary copper is 3·597 A.U.

5. *Summary.*

Colloidal copper was prepared by an electrical dispersion method, the dispersing medium being benzene or propyl alcohol. The particles were prevented from coming into contact with air by conducting the dispersing and centrifuging experiment *in vacuo*. The diamagnetic susceptibility (χ) of the samples was determined by a sensitive Curie method. The value for copper *en masse* was found to be 0·080. The χ value increased as the size of the particles was reduced, the critical diameter below which large changes occurred being 0·8 μ.

Honda and Shimizu have shown that cold-working in the case of copper gives rise to increased diamagnetism. They have pointed out that due to the expansion on cold-working of the metal, there is a decrease in the paramagnetic component due to the diminution of free electrons and an increase in the diamagnetic component due to the increased number of bound electrons. They explain that the lattice constant is a little greater in the surface layer than in the interior and suggest the analogy between cold-working and colloidalisation. These conclusions are verified in the case of copper. The

thickness of the surface layer appears to be about 300 A. U. and its diamagnetic susceptibility 0·200. On the basis of the theory of Honda and Shimizu, we obtain for the density of the superficial layer a value of 8·404 as against 8·943 for the mass metal. Attention is drawn to the experimental work of Thomson on electron diffraction from electrolytic copper, wherein larger lattice constants were obtained for surface layers.

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THE RAMAN SPECTRUM OF PHOSPHORUS.

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(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction.*

Bhagavantam[1] investigated the Raman effect with yellow phosphorus in the solid state using the green and yellow radiations of the mercury arc as the exciting lines. He gives the characteristic frequencies as 607 (6), 468 (3) and 374 (1); the figures in the brackets being the intensities as recorded with the 5460 Å. U. excitation. He has discussed his results theoretically,[2] considering the two alternate forms for the tetra-atomic molecule, namely, that of a square and of a tetrahedron respectively. The former model would give four different frequencies of oscillation, while the tetrahedron would give three frequencies. Accordingly, the experimental results are regarded as supporting the tetrahedral model for P_4 which is in agreement with the fact that the yellow phosphorus crystallises in the cubic system.[3] For the particular law of forces adopted, the frequencies should have the ratio $2 : \sqrt{2} : 1$; the fact that the observed frequencies deviate from this ratio is regarded as indicating that the force system in the molecule is more complicated than that assumed. In the present paper the Raman spectrum of yellow phosphorus has been critically studied with the substance in four different states: (1) vapour, (2) liquid, (3) solid and (4) solution in carbon disulphide. Such a comparative study is evidently of interest in order to ascertain the influence of the state of aggregation on the characteristic frequencies of the molecules, and has so far been made in the case of very few substances. In the present investigation, some additional bands have been recorded besides those reported by Bhagavantam and a small shift has been observed in the frequency of the most intense line as we pass from the solid to the liquid and to vapour.

2. *Experimental Arrangements and Results.*

The experimental arrangements were the same as those described in the previous communications of the author[4] in these *Proceedings*. Small

[1] Bhagavantam, S., *Ind. Jour. Phys.*, 1930, **5**, 35.
[2] Bhagavantam, S., *Ind. Jour. Phys.*, 1930, **5**, 73.
[3] Natta and Passerini, *Nature*, 1930, **125**, 707.
[4] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, 1935, **1**, 850.

transparent pieces of yellow phosphorus were kept immersed in distilled water and exposed in the vertical tube, the solid being kept at the room temperature by the circulation of cold water in an outer jacket surrounding the experimental tube. Liquid phosphorus was formed by the heating of the yellow crystals contained in an evacuated tube, by the heat of the mercury arc itself. The solution in carbon disulphide was prepared by dissolving clean pieces of yellow phosphorus in freshly distilled carbon disulphide contained in a closed tube during exposure. The arrangement for the vapour is shown in Fig. 1. A few bits of phosphorus were contained in a thick-

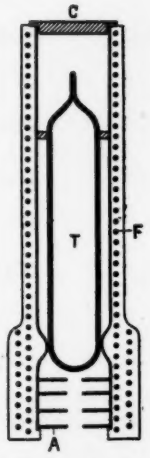

FIG. 1. T=Tube, F=Furnace, A=Aperture, C=Cap.

walled pyrex tube, which was evacuated, rendered moisture free, and sealed off. The tube was supported vertically as illustrated, inside another tube over which nichrome wire was wound in order to serve as an electric furnace. A few additional turns of heating coil at the lower end of the furnace prevented the condensation of the vapour in the bottom of the tube. Once the phosphorus was vaporised, it was found necessary to keep the temperature high enough in order to prevent the formation of red phosphorus. With a current of about 4·5 amperes in the heating coil, the temperature inside the tube remained almost steady at 450° C. A series of apertures were used on the observation side so that the reflection from the walls of the tube was completely eliminated.

The time of exposure was four hours for the solid, twelve hours for the liquid and the solution and six days for the vapour at a pressure of about 15 atmospheres. The spectrograms were measured with a Hilger Cross-Slide

Micrometer in comparison with an iron arc spectrum which was recorded in the centre of every plate.

TABLE I.

Solid Phosphorus (*Temperature* 30° C.).

Exciting line	Raman lines		$\Delta\nu$ in cm.$^{-1}$	Intensity
	λ	ν		
5790·5 ($\nu = 17265$)	6000·0	16662	603	3
,,	5950·6	16800	465	1
5769·6 ($\nu = 17328$)	5977·5	16725	603	3
,,	5928·3	16864	464	1
5460·7 ($\nu = 18308$)	5646·0	17706	602*	8
,,	5602·2	17845	463	4
,,	5573·3	17938	370(?)	0
4358·3 ($\nu = 22938$)	4476·0	22335	603	2
,,	4447·9	22477	461	1

* This line is followed by an unresolved wing.

TABLE II.

Liquid Phosphorus (*Temperature* 75° C.).

Exciting line	Raman lines		$\Delta\nu$ in cm.$^{-1}$	Intensity
	λ	ν		
5790·5	6001·5	16659	606	6
,,	5951·6	16800	465	3
5769·6	5979·0	16720	606	6
,,	5928·6	16863	465	3
5460·7	5647·4	17702	606	8
,,	5602·5	17844	464	4

TABLE III.

Phosphorus Vapour (Temperature 450° C.).

Exciting line	Raman lines		$\Delta\nu$ in cm.$^{-1}$	Intensity
	λ	ν		
5460·7	5649·5	17696	612	3
,,	5603·0	17843	465 (diffuse)	1

TABLE IV.

Solution in CS_2 (52%).

Exciting line	Raman lines		$\Delta\nu$ in cm.$^{-1}$	Intensity
	λ	ν		
5460·7	5664	17650	658	3
,,	5649	17697	611	8
,,	5603	17843	465	3

In addition to the lines tabulated above, a strong fluorescent band has also been recorded in all the four plates with its centre at 6400 Å. U. and extending from 6230 Å. U. to 6550 Å. U., which is evidently due to the phosphorus itself. The strong line at 602 in the solid is accompanied by a faint wing to the red side, which would probably resolve into a companion line at higher dispersions. The faint line at 374 reported by Bhagavantam[5] has appeared only as a faint darkening on the plates of the solid and the liquid and the author is, hence, unable to confirm the reality of that line.

The influence of change of state on the Raman lines is not shown to any marked extent. The line at 602 in the solid is shifted slightly towards a higher frequency while passing from the solid to the liquid and hence to the vapour, the variation in frequency being of the order of four wave-numbers from the solid to the liquid and six wave-numbers from the liquid to the vapour. The shift remains almost the same in the two states of the vapour and the solution. The line at 464 appears unshifted in all the four states;

[5] Bhagavantam, S., *Loc. cit.*

but in the case of vapour it has become slightly more diffuse. Only small variations in the frequency have been observed in the past in the case of the non-polar compounds like H_2 or O_2,[6] while the polar molecules like hydrochloric acid[7] give in general large shifts. In the case of sulphur, the author[8] has not been able to observe any change in the frequencies from the solid to the molten conditions. Hence we are led to conclude that the small shifts observed in phosphorus while passing from the solid to the vapour are only such as could be accounted for by the Lorentz-Lorentz forces and shows that the P_4 molecule is non-polar. It may also be of interest to mention that though the frequency shifts in the vapour and solution are almost identical, the spectrum of carbon disulphide itself is comparatively feeble.

In conclusion the author wishes to thank Prof. Sir C. V. Raman for his kind interest in the work.

Summary.

The Raman spectrum of yellow phosphorus as vapour, liquid, solid, and solution in carbon disulphide has been obtained. Only small changes in frequency are observed while passing from solid to liquid and to vapour, indicating the non-polar character of the molecule. The spectrum of carbon disulphide is rendered weak although the spectrum of phosphorus in solution comes out strongly. A strong fluorescent band extending from 6230 Å. U. to 6550 Å.U. has also been recorded in all cases.

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THE KINETICS OF HETEROGENEOUS ORGANIC REACTIONS: THE REACTION BETWEEN BENZYL CHLORIDE AND SOLID SILVER NITRATE.

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Introduction.

In connection with a systematic study which is being made in these laboratories on the kinetics of heterogenous organic reactions[1] we have investigated the reaction between solid silver nitrate and benzyl chloride in the absence of all solvents and diluents. No previous work of this type appears to have been carried out on the reaction. Burke and Donnan[2] (1904), Donnan and Potts[3] (1910) and Senter[4] (1910) investigated the reaction between silver nitrate and alkyl iodides in alcoholic and aqueous alcoholic solutions and have found the reaction to be complicated by the presence of the solvent.

Materials Used.

Silver Nitrate.—Experiments were carried out with Kahlbaum's "purest for analysis", Merck's "purest guaranteed reagent", and Johnson's "double crystallized" silver nitrate. It was found that all these different samples gave results agreeing within the experimental error. To obtain reproducible results, it was essential to have the particles of silver nitrate of average uniform size. This was accomplished in the following way:—

Silver nitrate was ground in a pestle and mortar in dim diffused light, and then sieved through a silk cloth of fine mesh to remove small particles, and then through a slightly bigger mesh. What passed through the second mesh was collected. The particles were examined under a microscope and the sieving repeated until they were of an average uniform size, and gave a standard rate of reaction under standard conditions. The standard reaction for medium size particles was:—

[1] *J. Phys. Chem.*, 1935, **39**, 727, 901, 907.
[2] *J. C. S.*, 1904, **85**, 555.
[3] *J. C. S.*, 1910, **97**, 1882.
[4] *J. C. S.*, 1910, **97**, 346.

Temperature	Benzyl chloride	Time of reaction	Initial silver nitrate	Silver nitrate reacting
35°C.±1°	5 c.c.	10 mts.	2 gm.	1·85±·05

The sieving cloths and the process of sieving were standardized before beginning the set of experiments.

Three different sizes of particles denoted "Small", "Medium" and "Large" were employed. No difficulty was experienced in preparing fresh samples of the sizes.

It was observed that the presence of moisture considerably inhibits the reaction (see Fig. 4). Hence the samples of silver nitrate were kept in the

	Small size S	Medium size M	Large size L
Mesh of fine sieve ..	L 0·019 cm.	L 0·028 cm.	L 0·048 cm.
	B 0·017 cm.	B 0·024 cm.	B 0·037 cm.
Mesh of coarse sieve ·	L 0·023 cm.	L 0·031 cm.	L 0·057 cm.
	B 0·017 cm.	B 0·026 cm.	B 0·049 cm.
Average weight of a particle ..	$1·216\times10^{-5}$ gm.	$4·272\times10^{-5}$ gm.	$4·145\times10^{-4}$ gm.
Number of particles per gm. ..	82402	23407	2412
Average volume of a particle ..	$2·795\times10^{-6}$c.c.	$9·82\times10^{-6}$ c.c.	$9·53\times10^{-5}$c.c.
Average dimensions of a particle ..	L 0·031 cm.	L 0·048 cm.	L 0·093 cm.
	B 0·019 cm.	B 0·03 cm.	B 0·055 cm.
	T 0·00474 cm.	T 0·00682 cm.	T 0·0186 cm.
Average surface area of a particle ..	0·00165 sq. cm.	0·00394 sq. cm.	0·0158 sq. cm.
Surface area of one gm. ..	136 sq. cm.	92·2 sq. cm.	38 sq. cm.

dark, in a desiccator over phosphorus pentoxide. At intervals the reaction velocities of these samples were checked in standard experiments.

The sizes of the meshes of different cloths, and the sizes and surface area of particles are given in the above table.

The average surface area of a particle was determined as follows:—

A fraction of a gram of the particles was weighed and the number of particles was counted. From this, the average weight of a particle and the number of particles per gram were calculated. Then about fifty particles were examined under a microscope. The shape of all these three types was observed to be cuboid. The length and breadth of each particle was measured under the microscope by means of a standard scale placed in the eye-piece. From this the average length L and the average breadth B of each particle were calculated. From the average weight of each particle, and the density of silver nitrate (4·35), the volume of each particle was determined. Hence from the knowledge of the volume and L and B, the average thickness T of each particle was calculated. The surface area was calculated from the formula $2(L \times B + L \times T + B \times T)$.

Benzyl Chloride.—Kahlbaum's benzyl chloride "purest" was used throughout the set of experiments. Its properties were not altered by fractionation under reduced pressure. The standard rate of reaction of a sample of benzyl chloride decreases on keeping for some weeks. The effect is marked with smaller amounts (less than one gram) of silver nitrate, where the impurity in the benzyl chloride is relatively more important. The decrease is probably due to the hygroscopic nature of benzyl chloride. Accordingly, it was preserved in small lots in amber-coloured bottles under anhydrous conditions.

Experimental Methods.

Benzyl chloride was measured by means of a burette, protected from moisture, into a small conical flask. It was confirmed that Jena-glass bottles gave the same result. A thermometer was fixed through the cork, and the flask was covered with black paper and was kept in an air thermostat adjusted to 35° ± ·2°C.

When the bottle attained the required initial temperature, sieved silver nitrate previously weighed in a weighing bottle and kept in a desiccator was added and the stop-watch started. The bottle was shaken by hand to mix the reactants thoroughly—this shaking is necessary—and it was then placed on the shaker which was also fixed in the thermostat, and the latter was started. The speed of rotation of the shaker was kept constant by means of a rheostat in the circuit of the motor. It was confirmed that variation of

speed of shaking between 75 and 180 revolutions per minute did not affect the rate of reaction (*see* Tables IV and V).

After a definite interval of time, the bottle was removed from the shaker, the temperature was read and the silver salts were rapidly filtered through a gooch crucible and washed free from benzyl chloride with dry ether or acetone. The receiver was then changed and the residual silver nitrate was washed down with distilled water. This washing was titrated with standard ammonium thiocyanate. In this way the amount of silver nitrate unused was obtained. This *minus* the initial amount gave the silver nitrate used.

In some experiments the results were checked by gravimetric estimation of the residual silver chloride. The volumetric and gravimetric results agreed excellently.

TABLE I.

Small Size Particles.

$AgNO_3$ initial	Benzyl chloride	Time	Temp. initial	Temp. final	$AgNO_3$ left	$AgNO_3$ used	K
gm.	c.c.	mts.	°C.	°C.	gm.	gm.	
1	5	3	34	35	0·387	0·613	0·0020
1	5	5	34	35·3	0·18	0·82	0·0019
1	5	7	34	35·5	0·033	0·967	0·0021
1	20	3	34	35	0·404	0·596	0·0019
1	20	5	34	35	0·194	0·806	0·0019
1	20	7	34	35·3	0·072	0·928	0·0018
3	5	3	33	37·5	0·73	2·27	0·0027
3	5	5	33	35·5	0·30	2·70	0·0025
3	5	7	33	37	0·04	2·96	0·0024
3	20	3	34	36	1·065	1·935	0·0021
3	20	5	34	36	0·27	2·73	0·0024
3	20	7	34	35·5	0·065	2·935	0·0023

Control of Reaction Temperature.

The reaction is exothermic and with the larger amounts of silver nitrate the rise in temperature is marked. As the heat of combustion of benzyl nitrate has not been determined, the heat change in the reaction cannot be calculated.

After a number of experiments it was found that by starting a little below 35° C. and by adjusting a wet cloth of suitable dimensions around or at the bottom of the bottle it was usually possible to keep the average temperature of the reaction close to 35° C. The degree of the wetness of the cloth and the extent to which the bottle was covered with it for different systems was determined in preliminary experiments. It was confirmed that the reaction is not sensitive to small temperature variations.

Experimental Results and Discussion.

TABLE II.

Medium Size Particles.

$AgNO_3$ initial	Benzyl chloride	Time	Temp. initial	Temp. final	$AgNO_3$ left	$AgNO_3$ used	K
gm.	c.c.	mts.	°C.	°C.	gm.	gm.	
1	5	2·5	35	35·7	0·60	0·40	0·0020
1	5	5	35	34	0·32	0·68	0·0020
1	5	7·5	35	37	0·164	0·836	0·0020
1	5	10	35	36	0·07	0·93	0·0019
1	10	2·5	35	36·6	0·62	0·38	0·0019
1	10	5	35	34·5	0·37	0·63	0·0018
1	10	7·5	35	35	0·19	0·81	0·0018
1	10	10	35	35·3	0·07	0·93	0·0019
1	20	2·5	35	35	0·65	0·35	0·0017
1	20	5	35	35·6	0·352	0·648	0·0019
1	20	7·5	35	35·6	0·144	0·856	0·0020
1	20	10	35	37	0·07	0·93	0·0019
2	5	2·5	34	37	1·19	0·81	0·0020
2	5	5	34	37	0·66	1·34	0·0020

TABLE II—(*Contd.*)
Medium Size Particles.

$AgNO_3$ initial	Benzyl chloride	Time	Temp. initial	Temp. final	$AgNO_3$ left	$AgNO_3$ used	K
gm.	c.c.	mts.	°C.	°C.	gm.	gm.	
2	5	7·5	34	36·6	0·29	1·71	0·0020
2	5	10	34	38	0·10	1·90	0·0020
2	10	2·5	34	35	1·30	0·70	0·0017
2	10	5	34	36·5	0·70	1·30	0·0019
2	10	7·5	34	36	0·28	1·72	0·0021
2	10	10	34	36	0·20	1·80	0·0017
2	20	2·5	34	35·4	1·25	0·75	0·0019
2	20	5	34	36	0·70	1·30	0·0019
2	20	7·5	34	35·5	0·36	1·64	0·0019
2	20	10	34	35·3	0·20	1·80	0·0017
3	5	2·5	33	36	1·70	1·30	0·0022
3	5	5	33	36·5	0·80	2·20	0·0023
3	5	7·5	33	36·5	0·40	2·60	0·0021
3	5	10	33	37	0·26	2·74	0·0018
3	10	2·5	33	35·3	1·70	1·30	0·0022
3	10	5	33	35·5	0·86	2·14	0·0022
3	10	7·5	33	36·3	0·40	2·60	0·0021
3	10	10	33	37·5	0·25	2·75	0·0018
3	20	2·5	34	36	1·80	1·20	0·0020
3	20	5	34	36	1·00	2·00	0·0020
3	20	7·5	34	38	0·40	2·60	0·0021
3	20	10	34	37	0·25	2·75	0·0018

TABLE III.
Large Size Particles.

$AgNO_3$ initial	Benzyl chloride	Time	Temp. initial	Temp. final	$AgNO_3$ left	$AgNO_3$ used	K
gm.	c.c.	mts.	°C.	°C.	gm.	gm.	
1	5	5	34	35	0·678	0·322	0·0020
1	5	15	34	36	0·24	0·76	0·0020
1	5	25	34	35·7	0·096	0·904	0·0017
1	20	5	35	35	0·678	0·322	0·0020
1	20	15	35	33·5	0·274	0·726	0·0018
1	20	20	35	34	0·15	0·85	0·0019
1	20	25	35	35·2	0·096	0·904	0·0017
3	5	5	34	35	2·08	0·92	0·0018
3	5	15	34	35·5	0·678	2·322	0·0021
3	5	20	34	35	0·46	2·54	0·0018
3	5	25	34	34	0·323	2·677	0·0016
3	20	5	34	33·6	2·10	0·90	0·0018
3	20	15	34	35·5	0·654	2·346	0·0021
3	20	25	34	33·5	0·186	2·814	0·0019

Tables I, II, III, and Figs. 1, 2 and 3 give the results of the experiments. It will be seen that the rate of the reaction is independent of the initial amount of benzyl chloride. That is to say, if we take two grams of silver nitrate, it matters not as far as the rate of reaction is concerned whether we start with 5 c.c., 10 c.c. or 20 c.c. of benzyl chloride. This is a striking result, since with smaller amounts of benzyl chloride, the concentration of benzyl nitrate in the liquid reaction mixture increases rapidly. One would expect therefore the rate of reaction to fall off more quickly than with larger initial quantities of benzyl chloride.

We can explain this result by assuming that benzyl chloride is adsorbed on the surface of the silver nitrate crystals, and that the amount of adsorption does not depend greatly on the concentration of benzyl chloride in the

mixture. There is therefore always a constant concentration of benzyl chloride on the silver nitrate surface, and the rate of reaction is consequently proportional to the surface of silver nitrate present, so that during an experiment the interface between silver nitrate and silver chloride will travel inwards through the crystal at a constant linear rate.

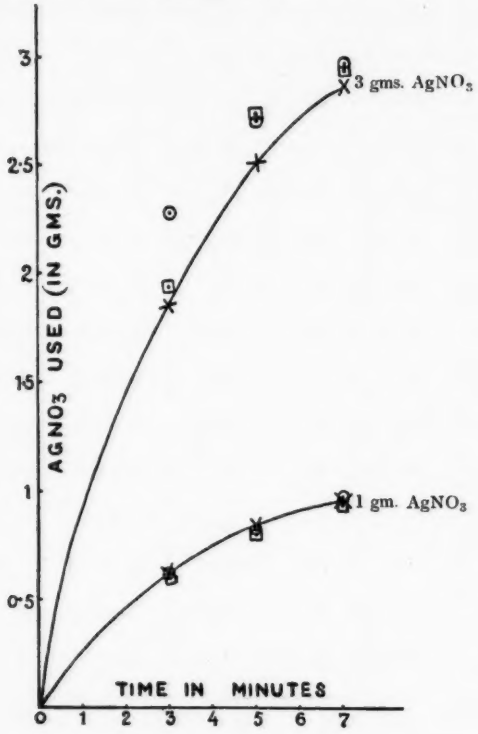

FIG. 1. Small Size $AgNO_3$ Particles.

Benzyl Chloride + $AgNO_3$

⊙ 5 c.c. + 1 & 3 gms.

⊡ 20 c.c. + ,,

× Calculated from K = 0·002

This type of reaction has been found by Spencer and Topley[5] (1929), to apply to the decomposition of silver carbonate. They point out that an equation of the type deduced below applies strictly only to particles of uniform size, but is approximately true as an average result when factors such

[5] *J. C. S.*, 1929, 2633.

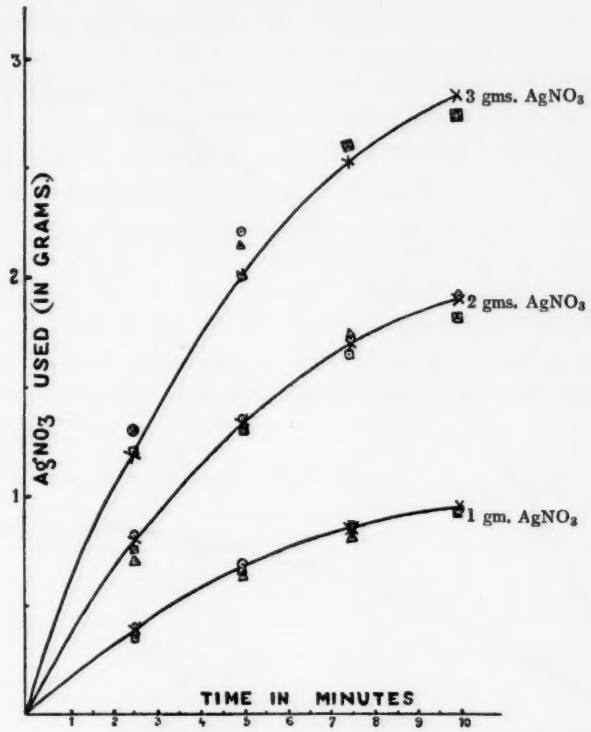

FIG. 2. Medium Size $AgNO_3$ Particles.

Benzyl Chloride + $AgNO_3$

⊙ 5 c.c. + 1, 2 & 3 gms.

◭ 10 c.c. + ,,

⊡ 20 c.c. + ,,

× Calculated from K = 0·002

as irregular shape and different reaction rates parallel to different crystal axis are averaged over the large number of particles contained in the reactive material. They also point out that reactants can be assumed to pass to and from the crystal interface by means of micro-fissures in the crystals.

With substances with large molecules such as benzyl chloride and benzyl nitrate this hypothesis is not so probable. On the other hand the silver chloride formed around the silver nitrate particles may have a loose porous form, that is to say, a continuous crystal lattice is not formed but rather an agglomeration of particles.

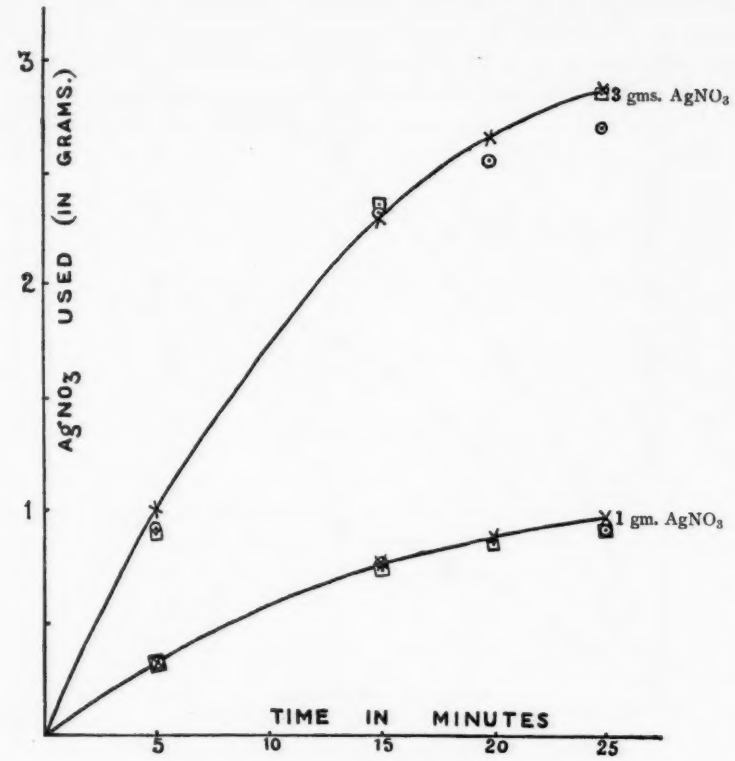

FIG. 3. Large Size $AgNO_3$ Particles.

Benzyl Chloride + $AgNO_3$
⊙ 5 c.c. + 1 & 3 gms.
⊡ 20 c.c. + ,,
× Calculated from K= 0·002

It must also be emphasised that while in many liquid phase heterogeneous reactions, the chemical effect is obscured by conditions of physical transport, yet in many other instances the chemical effect predominates. Roller[6] (1935) cites a number of reactions in which diffusion does not play a part, *e.g.*, Schmidt and Durau[7] (1924) showed that the rate of solution of glass in alkali is independent of the rate of stirring, and the concentration of alkali, but depends on the surface of the glass exposed. In our experiments the con-

[6] *J. Phys. Chem.*, 1935, **39**, 221.
[7] *Z. Phys. Chem.*, 1924, **108**, 128.

centration of benzyl chloride in the reacting medium is always high being never less than 60% by weight. This may tend to minimise diffusion effects, since there are always a large number of molecules near the reacting surface.

The real test of the hypothesis, however, is to examine how far the corresponding kinetic equation can reproduce the experimental results.

We deduce the kinetic equation as follows :—

Let A be the intial amount of silver nitrate in gms. and let X be the amount left at a time t. Let K be the number of gms. of silver nitrate reacting per sq. cm. of silver nitrate surface per second. Let $\bar{S}$ be the surface in sq. cms. of one gm. of the silver nitrate initially used.

Now if the silver nitrate particles be taken on an average to be spheres of the calculated surface area, the surface of the X gm. remaining after time t will be equal to

$$\frac{(\bar{S}A)\ X^{\frac{2}{3}}}{A^{\frac{2}{3}}} = \bar{S}\ A^{\frac{1}{3}} X^{\frac{2}{3}}$$

Hence

$$-\frac{dX}{dt} = K\bar{S}A^{\frac{1}{3}} X^{\frac{2}{3}} \quad \ldots\ldots(1)$$

$$-dt = \frac{dX}{K\bar{S}A^{\frac{1}{3}}X^{\frac{2}{3}}} \quad \ldots\ldots(2)$$

$$t = \frac{3A^{\frac{1}{3}}}{K\bar{S}A^{\frac{1}{3}}}\left(1 - \frac{X^{\frac{1}{3}}}{A^{\frac{1}{3}}}\right) \quad \ldots\ldots(3)$$

$$K = \frac{3}{t\bar{S}}\left(1 - \frac{X^{\frac{1}{3}}}{A^{\frac{1}{3}}}\right) \quad \ldots\ldots(4)$$

The values of K calculated from (4) are shown in Tables I, II and III and the constancy of the values indicates the general correctness of the assumed mechanism. A more stringent test is to use (4) to calculate the experimental results.

Examination of all experimental results indicate that K has an average value of 0·002. Hence as the small size (S) of silver nitrate used has a surface area per gm. of 136 sq. cm. we have for this sample the kinetic equation

$$0{\cdot}002 = \frac{3}{t(136)}\left(1 - \frac{X^{\frac{1}{3}}}{A^{\frac{1}{3}}}\right) \quad \ldots\ldots(5)$$

For the medium size (M) with the surface area per gm. of 92·2 sq. cm. we have

$$0{\cdot}002 = \frac{3}{t(92{\cdot}2)}\left(1 - \frac{X^{\frac{1}{3}}}{A^{\frac{1}{3}}}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

And for the large size (L) with the surface area per gm. of 38 sq. cm.

$$0{\cdot}002 = \frac{3}{t(38)}\left(1 - \frac{X^{\frac{1}{3}}}{A^{\frac{1}{3}}}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

From (5), (6) and (7), X has been calculated for various values of t, and the results are shown by full lines in Figs. 1, 2 and 3.

It will be seen that the equation reproduces well the experimental results. The agreement is all the more striking when it is remembered that for all these three results involving three different sizes of silver nitrate only one constant $K = 0{\cdot}002$ has been used.

It should be noted however that with quantities of silver nitrate below 1·5 gm. it was more difficult to get constant result, low rates of reaction being sometimes obtained. It is believed that this effect is due to impurity in the benzyl chloride, but it is hoped to investigate the matter further.

Effect of Speed of Shaking.

A few experiments were made to see whether the change in the speed of shaking has any effect on the velocity of reaction. The speeds employed were 180, 120 and 75 revolutions per minute of the shaker. The general experimental technique was the same as described before. The results are given in the Tables IV and V.

It will be seen from the results that change in the speed of shaking within limits has no effect on the velocity of reaction.

Effect of Water.

It has already been stated that moisture inhibits the reaction to a considerable extent. A few experiments were carried out to study quantitatively the effect of water on the rate of reaction. Distilled water was added to benzyl chloride before the reaction. Otherwise the experimental procedure was the same as before.

The systems studied were

Benzyl chloride	Silver nitrate	H_2O
5 c.c.	2 gm.	0·01 c.c.
5 ,,	2 ,,	0·05 ,,
5 ,,	2 ,,	0·10 ,,

TABLE IV.

Results with Variation in the Shaker Speed.

$AgNO_3$ initial	Benzyl chloride	Time	No. of shaker revolutions per mt.	$AgNO_3$ left gm.	$AgNO_3$ used gm.	K
1 gm.	5 c.c.	2·5 mts.	180	0·62	0·38	0·0017
			120	0·56	0·44	0·0023
			75	0·65	0·35	0·0017
1 gm.	5 c.c.	5 mts.	180	0·37	0·63	0·0018
			120	0·25	0·75	0·0024
			75	0·31	0·69	0·0021
1 gm.	5 c.c.	10 mts.	180	0·05	0·95	0·0020
			120	0·03	0·97	0·0022
			75	0·05	0·95	0·0020

TABLE V.

Results with Variation in the Shaker Speed.

$AgNO_3$ initial	Benzyl chloride	Time	No. of shaker revolutions per mt.	$AgNO_3$ left gm.	$AgNO_3$ used gm.	K
1 gm.	10 c.c.	2·5 mts.	180	0·60	0·40	0·0020
			120	0·62	0·38	0·0017
			75	0·58	0·42	0·0022
1 gm.	10 c.c.	5 mts.	180	0·33	0·67	0·0020
			120	0·28	0·72	0·0022
			75	0·30	0·70	0·0021
1 gm.	10 c.c.	10 mts.	180	0·07	0·93	0·0019
			120	0·04	0·96	0·0021
			75	0·09	0·91	0·0018

The results are shown graphically in Fig. 4. The effect of 0·01 c.c. of water on the reaction of 5 c.c. of benzyl chloride (0.18% by weight) is marked. This effect increases with the amount of water added.

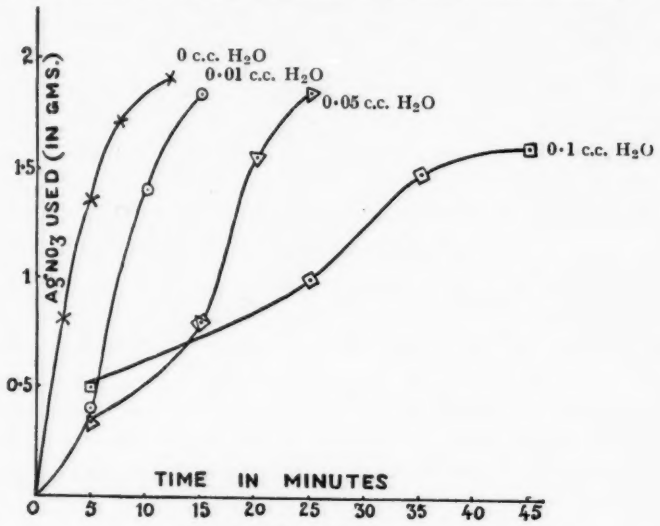

FIG. 4. Effect of H_2O.

	Benzyl Chloride	+ $AgNO_3$	+ H_2O
×	5 c.c.	+ 2 gms.	+ 0 c.c.
●	,,	+ ,,	+ 0·01 c.c.
◭	,,	+ ,,	+ 0·05 c.c.
▣	,,	+ ,,	+ 0·1 c.c.

Summary.

(1) The kinetics of the reaction between benzyl chloride and solid silver nitrate has been studied in the absence of solvents and diluents.

(2) The reaction is independent of the amount of benzyl chloride, but is proportional to the surface of silver nitrate present.

(3) The reaction has been studied with particles of three different sizes, and it has been shown that all the experimental results can be reproduced by the kinetic equation derived on the assumption that the rate of reaction depends only on the surface of silver nitrate present.

(4) The velocity of reaction is independent of the speed of shaking.

(5) Water inhibits the reaction; the effect of 0·18% by weight of benzyl chloride taken is marked and this effect increases with the amount of water added.

THE RAMAN SPECTRA OF DIOXANE AND TETRALIN.

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Received August 23, 1935.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

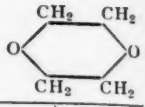
In spite of the fact that organic compounds generally give rather complicated Raman spectra, the extensive researches in this field carried out in the last few years have enabled, in many cases, the modified lines to be classified into groups which can be identified as due to certain characteristic groups or chemical bonds in the molecule. In order to interpret the results in relation to the molecular structure, it is important to obtain the Raman spectra of the compounds studied as completely as possible. The simple ring compounds repeatedly investigated by several workers include benzene, cyclohexane and naphthalene. But comparatively little work has been done in other cyclic compounds possessing a somewhat similar structure. The present paper gives the results obtained by the author with dioxane and tetralin.

Explanation of Symbols.

Symbol	Wavelength	Wavenumber
a	3650	27358
b	3655	27353
d	4047	24705
e	4078	24516
f	4339	23039
g	4348	22995
h	4358	22938

TABLE I.

The Raman frequencies of Dioxane from 4047 Å. U.—5100 Å. U.



No.	Raman lines		$\Delta\nu$ in cm.$^{-1}$	Intensity		Assignment
	λ	ν		Without filter	With filter	
1	4062·5	24609	2779	1	..	*a*
2	4067·3	24580	2773	0	..	*b*
3	4076·6	24523	2863	4	..	*a*
4	4086·8	24462	243	2	..	*d*
5	4092·7	24427	2961	6*b*	..	*a*
6	4099·5 (double)	24387	$\overline{1449}$	3*b*	1	*h*
7	4111·7	24314	3075	1	..	*a*
8	4116·6	24285	421	0	..	*d*
9	4118·5	24273	433	3	..	*d*
10	4127·6	24220	485	5	..	*d*
11	4140·1	24147	$\overline{1209}$	0	..	*h*
12	4148·7	24097	419	0	..	*e*
13	4156·8	24050	466	0*b*	..	*e*
14	4188·5	23868	837	8*sh*	2	*d*
15	4191·1	23854	851	1*sh*	..	*d*
16	4204·7	23771	$\overline{835}$	3	1	*h*
17	4207·7	23759	946	0	..	*d*
18	4220·2	23689	1016	8	0	*d*
19	4221·4	23682	834	2	..	*e*
20	4237·1	23596	1109	3	..	*d*

TABLE I (*contd.*)

No.	Raman lines		$\Delta\nu$ in cm.$^{-1}$	Intensity		Assignment
	λ	ν		Without filter	With filter	
21	4240·3	23576	1129	3	..	*d*
22	4255·0	23495	1210	0	..	*d*
23	4256·8	23485	1221	5	0	*d*
24	4272·5	23399	1306	6	0	*d*
25	4277·4	23372	1333	2	..	*d*
26	4291·1	23297	1219	1	..	*e*
27	4297·8	23261	1444	6	0	*d*
28	4306·0	23249	1455	0	..	*d*
29	4307·9	23207	1299	0	..	*e*
30	4393·0	22757	181?	0	..	*h*
31	4441·0	22512	426	0	0	*h*
32	4442·3	22504	434	2	2	*h*
33	4451·6	22458	480	4	3	*h*
34	4523·2	22102	836	10*sh*	8	*h*
35	4525·6	22090	848	0	0	*h*
36	4535·2	22044	2662	1	..	*d*
37	4546·7	21988	2718 950	3 0	0	*d* *h*
38	4554·5	21950	2756	0	..	*d*
39	4560·3	21922	2783 1006	6	4	*d* *h*
40	4576·3	21846	2860 1109	8	2	*d* *h*
41	4582·2	21818	2888 1120	3	1	*d* *h*

TABLE I (*concld.*)

No.	Raman lines		$\Delta\nu$ in cm.$^{-1}$	Intensity		Assignment
	λ	ν		Without filter	With filter	
42	4597·7	21744	2962	10	1	*d*
43	4600·8	21729	1209	1	..	*h*
44	4603·4	21717	1221	6	4	*h*
45	4616·8	21654	2863	3	..	*e*
46	4621·4	21632	3074 1306	8	4	*d* *h*
47	4626·2	21610	1328	2	1	*h*
48	4640·3	21544	2973	3(*b*)	..	*e*
49	4650·8	21496	1442	8	6	*h*
50	4652·6	21487	1451	0	0	*h*
51	4929·6	20279	2659	1	1	*h*
52	4944·5	20220	2718	1	1	*h*
53	4960·7	20153	2785	3	2	*h*
54	4980·9	20071	2867	8	6	*h*
55	4986·1	20050	2888	2	1	*h*
56	4991·6	20027	2968	1	0	*g*
57	5006·0	19970	2968	8*b*	8	*h*
58	5032·8	19864	3074	1	0	*h*

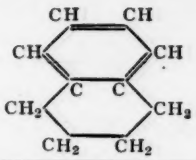
2. *Experimental Arrangements and Results.*

The experimental set up was the same as that previously used in the investigations of the author.[1] The two liquids used in this investigation were those used for the measurements of dipole moments at the Institute

[1] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, 1935, **1**, 850.

TABLE II.

The Raman frequencies of Tetralin from 4047 Å. U.—5100 Å. U.



No.	Raman lines		$\Delta\nu$ in cm.$^{-1}$	Intensity		Assignment
	λ	ν		Without filter	With filter	
1	4071·7	24553	153	6	1	*d*
2	4089·1	24448	258	2	0	*d*
3	4095·5	24410	2944	1	..	*b*
4	4104·6	24356	$\overline{1418}$	0	..	*h*
5	4117·6	24279	427	2	0	*d*
6	4119·9	24266	440	2	..	*d*
7	4123·2	24246	460	0	..	*d*
8	4130·8	24202	504	1	..	*d*
9	4139·9	24148	557	0	..	*d*
10	4143·8	24128	578	3	..	*d*
11	4164·6	24005	701	1	..	*d*
12	4168·1	23985	721	8	2	*d*
13	4176·5	23946	760	0	..	*d*
14	4181·8	23906	800	1	..	*d*
15	4184·5	23891	815	2	..	*d*
16	4200·8	23798	908	2	..	*d*
17	4214·0	23724	982	0	..	*d*
18	4223·2	23672	1034	10	3	*d*
19	4228·0	23645	1061*	0	..	*d*

* An asterisk mark against some of the frequency numbers shows that they possess a doublet structure.

TABLE II (*contd.*)

No.	Raman lines		$\Delta\nu$ in cm.$^{-1}$	Intensity		Assignment
	λ	ν		Without filter	With filter	
20	4239·0	23584	1122	0	..	*d*
21	4245·8	23546	1160	1	..	*d*
22	4253·1	23506	1200	8	2	*d*
23	4258·4	23476	1230*	0	..	*d*
24	4268·2	23421	1285	3	..	*d*
25	4277·0	23369	1336	3	..	*d*
26	4279·5	23360	$\overline{422}$	0	2	*h*
27	4285·7	23327	1379	2	..	*d*
28	4293·8	23278	1427	6	1	*d*
29	4298·4	23258	1448	1	..	*d*
30	4307·9	23207	1499	0	..	*d*
31	4309·7	23197	$\overline{259}$	1	2	*h*
32	4322·0	23130	1575	0	..	*d*
33	4326·6	23106	1600	8	2	*d*
34	4329·3	23092	$\overline{154}$	4	4	*h*
35	4387·9	22784	154	5	8	*h*
36	4408·1	22680	258	3	4	*h*
37	4409·9	22670	268	..	0	*h*
38	4440·0	22511	427	3	6	*h*
39	4443·1	22500	438	..	0	*h*
40	4446·0	22486	457	1	4	*h*

* An asterisk mark against some of the frequency numbers shows that they possess a doublet structure.

TABLE II (*contd.*)

No.	Raman lines		$\Delta\nu$ in cm.$^{-1}$	Intensity		Assignment
	λ	ν		Without filter	With filter	
41	4455·4	22438	505	2	5	*h*
42	4467·0	22380	558	0	1	*h*
43	4470·5	22363	575	3	4	*h*
44	4495·0	22241	697	1	1	*h*
45	4499·6	22218	720	8	10	*h*
46	4508·1	22176	762	0	0	*h*
47	4515·8	22138	800	0	1	*h*
48	4518·7	22124	814	1	2	*h*
49	4537·0	22035	903	..	0	*h*
50	4544·1	22004	1035	0	0	*f*
51	4552·7	21959	1035 979	0	2	*g*, *h*
52	4560·3	21903	1035	8	10	*h*
53	4570·3	21874	1064*	3	2	*h*
54	4576·9	21843	2863	1	..	*d*
55	4584·5	21806	2902	1	..	*d*
56	4590·5	21778	2930 1160	4*b*	4	*d*
57	4594·0	21762	2943	0	0	*d*
58	4601·4	21726	1202	5	6	*h*
59	4607·0	21704	1234	0	1	*h*
60	4617·1	21653	3052 1285	6	3	*d*, *h*
61	4627·8	21602	1336	1	2	*h*

TABLE II (*concld.*)

No.	Raman lines		$\Delta\nu$ in cm.$^{-1}$	Intensity		Assignment
	λ	ν		Without filter	With filter	
62	4636·3	21563	1383	1	2	*h*
63	4647·4	21511	1427	6	6	*h*
64	4652·2	21489	1449	1	2	*h*
65	4662·8	21440	1498	0	0	*h*
66	4680·8	21362	1576	2	2	*h*
67	4685·1	21339	1599	3	4	*h*
68	4980·8	20071	2867	3	3	*h*
69	4989·8	20035	2903	1	1	*h*
70	4993·7	20020	2918	0	0	*h*
71	4998·3	20001	2937	6	6	*h*
72	5018·7	19920	3008	1	1	*h*
73	5025	19892	3046	10	10	*h*

and the author's thanks are due to Dr. M. A. Govinda Rau for kindly permitting the use of the extra-pure substances which he had carefully prepared for his work. In order to facilitate the proper assignment of the excited lines, spectrograms were taken with and without filters. An alcoholic solution of *p*-nitro-toluene was found to be an efficient filter which cut off almost completely the 4046 radiations while transmitting the 4358 radiations of the source with maximum intensity. For dioxane, an alkaline solution of *o*-cresolpthalin helped to clear up the 4916 region considerably. The filter was contained in an outer jacket surrounding the experimental tube as in Fig. 1. It would be of interest to mention that tubes with almost perfectly flat ends could be easily made in pyrex glass with the outer tube fused to the bottom and supported with a few spokes dug into its walls at the top. In order to prevent the evaporation of the filter solution when the tube was placed close to the arc, the top end was closed with plaster of Paris through which two small tubes were passed for the introduction of the solution. The

TABLE III.

The intensities given in the brackets are for the 4358 *excitations.*

Dioxane		Tetralin			Cyclohexane	Benzene
Author	Villars	Author	Mukerji	Bonino and Cella	Krishnamurti	Grassman and Weiler (Incomplete)
181(0)?	..	154(8)	162(3)	158(4)	..	..
243(1)	..	259(4)	265(2)	265(3)	381($\frac{1}{2}$)	
	291(0)	268(0)	..	..	..	
425(0)	..	427(6)	430(4)	432(2)	425(1)	404(1)
		439(0)	..	..		
433(2)	434(00)	459(4)	..	..		
482(4)	519(00)	505(5)	511(3)	513(3)		
		558(1)	561(2)	567(2)		
		577(4)	582(3)	585(3)		607(8)
		699(1)	699(2)	..	695(0)	692(1)
		720(10)	723(5)	724(4)		
		761(0)	752(1)	759(1)		781(0)
837(8)	837(4)	800(1)	..	..	804(10)	802(0)
849(1)	..	814(2)	814(2)	815(2)		824($\frac{1}{2}$)
			839(0)	848(0)		849(4)
		905(0)				
946(0)	..	980(1)	..	..		984(2)
						992(15)
1012(6)	..	1035(10)	1037(7)	1038(5)	1028(8)	1034(1)
		1063(3)	..	..		
1109(3)	..	1122(0)	..	..		
	1117(1)					
1124(3)		1163(4)	1174(0)	1160(1)	1156(1)	1176(4)
1209(1)	..	1201(6)	1205(6)	1204(4)		
1221(5)	1214(1)	1232(1)	..	..	1266(5)	
		1285(3)	1283(1)	1283(2)		1285(0)
1306(8)	..	..	..	..	..	..
1328(2)	..	1336(2)	..	1340(1$\frac{1}{2}$)	1344($\frac{1}{2}$)	1326($\frac{1}{2}$)
1444(8)	1442(2)	1427(6)	1433(3)	1433(3)	1444(5)	1403(2)

TABLE III (*contd.*)

Dioxane		Tetralin			Cyclohexane	Benzene
Author	Villars	Author	Mukerji	Bonino and Cella	Krishnamurti	Grassman and Weiler (Incomplete)
1451(1)	..	1448(2)	1458(5)	1456(3)		1449($\frac{1}{2}$)
		1499(0)	..	..		1480(0)
		1575(2)	1582(3)	1583(3)		1585(12)
		1600(4)	1602(3)	1602(3)		1606(8)
2660(1)	..	..	..	..	2662(1)	2615(2)
2718(1)	2720(00)	..	..	..		
2784(3)	..	..	..	..		
2863(8)	2864(3)	2865(4)	2865(4)	2862(2$\frac{1}{2}$)	2852(8)	..
2888(2)	..	2902(1)	..	..	2889(1)	..
2968(10)*b*	2967(3)	2937(6)	2940(4)	..	2922(8)	2949(4)
		3008(1)	..	..		3049(8)
3064(1)	..	3049(10)	3046(5)	3049(5)		3064(12)

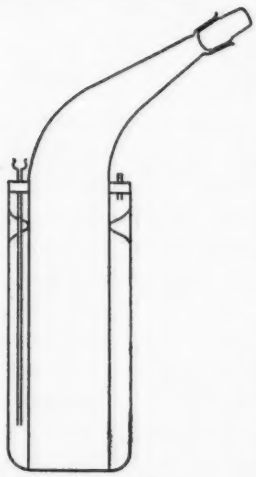


FIG. 1.

spectrograms were measured as usual and the results are tabulated in Tables I and II. The photographs are also reproduced in the accompanying plates. Dioxane was comparatively a poor scattering medium and an exposure of forty hours was required to bring out all the lines in its spectrum without any filter. Tetralin gave an intense picture at an exposure of nine hours; but in this case a continuous spectrum was also present.

3. *Discussion of Results.*

(*a*) *Dioxane.*—Except for a short report on the principal Raman lines by Villars,[2] this compound has not been studied in any great detail. From the point of view of the Raman effect this is an interesting compound, for it affords the unique example of a molecule possessing a structure similar

[2] Villars, *Jour. Amer. Chem. Soc.*, 1930, **52**, 4612.

to that of cyclohexane, but with two of the methylene groups replaced by oxygen atoms. As can be seen from the first column in Table III, the spectrum of dioxane consists of twenty-four lines of which fourteen have been observed for the first time. The author has been fortunate to be able to examine the cyclohexane plate of Krishnamurti[3] side by side with the latter and the comparison of the two reveals the following facts :—

(1) Both the compounds give only feeble wings accompanying the Rayleigh lines.

(2) All the important lines of cyclohexane appear more or less in the same position in dioxane.

(3) The region between 2863 and 2968 is covered by a band in both the cases which is attributed to the rotational spectrum accompanying the vibrational line due to C-H linkage.

(4) The wing structure of 1444 of cyclohexane is resolved into a close companion line in dioxane.

The outstanding differences in the two spectra are the following :—

(1) An intense line at 1306 (marked by the arrow in the accompanying plate) which is absent in cyclohexane, is one of the fundamental lines in dioxane and this is to be attributed to the oscillation of the group O $\begin{smallmatrix} CH_2 \\ \diagdown \\ \diagup \\ CH_2 \end{smallmatrix}$.

(2) The line due to the symmetrical oscillation of the carbons in cyclohexane at 804 is shifted to a higher frequency 837 in dioxane, and the lines due to C-H from 2852 and 2938 to 2863 and 2968 respectively.

(3) All the other lines belonging to C-C or CH_2 are shifted in the opposite direction.

(4) The line at 425 which is assumed to be one of the characteristic lines of the cyclohexane nucleus, is resolved into three lines in dioxane.

(5) There is a group of lines present in dioxane at about 2750 which is not present in cyclohexane and they may be explained partly as arising from the combination of 1444 and 1306.

(6) The intense doublet due to $C=H_2$ in cyclohexane at 2922 and 2938 appears as a single broad line at 2968 in dioxane.

It is clear from the above that dioxane possesses a structure similar to that of cyclohexane and its vibrations are modified to some extent by the presence of the two oxygen atoms in the place of two CH_2 groups in the ring.

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[3] Krishnamurti, P., *Ind. Jour. Phys.*, 1932, **6**, 543.

The presence of a weak line at 3064 which is characteristic of the aromatic linkage shows besides that it represents the transition between the aromatic and the aliphatic ring compounds.

(*b*) *Tetralin.*—This has been studied in great detail first by Bonino and Cella[4] and quite recently by Mukerji.[5] These authors have pointed out the great similarity of its spectrum to those of cyclohexane and naphthalene. The results given by them are in fair agreement with those of the author. As can be seen from Table III new lines have been observed at 268, 439, 459, 800, 905, 980, 1063, 1122, 1232, 2902 and 3008. The frequency shifts of cyclohexane and of benzene[6] are also given for comparison. The new points that have been observed by the author in the spectrum of tetralin besides those reported by the previous investigators, are the following :—

(1) The line at 1440 due to the deformation oscillation of CH_2 has been shifted slightly to a shorter wavelength and has been followed by a companion as in dioxane.

(2) The line at 425 has been split up into three lines as in dioxane.

(3) The continuous spectrum between 2865 and 2937 in cyclohexane and dioxane is present weakly also in tetralin and thus appears to be characteristic of the molecules of the cyclohexane type.

(4) The wings accompanying the Rayleigh lines are as prominent as in benzene.

(5) The important lines in the benzene spectrum at about 1600 due to C=C and above 3000 due to the aromatic CH appear also in tetralin.

(6) The line at 3046 shows a prominent wing on either side.

This similarity to the spectrum of cyclohexane on the one hand and of benzene on the other suggests that the molecule of tetralin is made up of one completed cyclohexane nucleus and one incomplete benzene nucleus.

In conclusion the author wishes to record his thanks to Sir C. V. Raman for his interest in the work.

Summary.

The Raman spectra of dioxane and tetralin have been obtained using the filter technique. The spectrum of dioxane consists of twenty-four lines of which fourteen are reported for the first time and resembles closely that of cyclohexane. Tetralin has also given eleven new lines. The results obtained are discussed with reference to the structure of the molecules.

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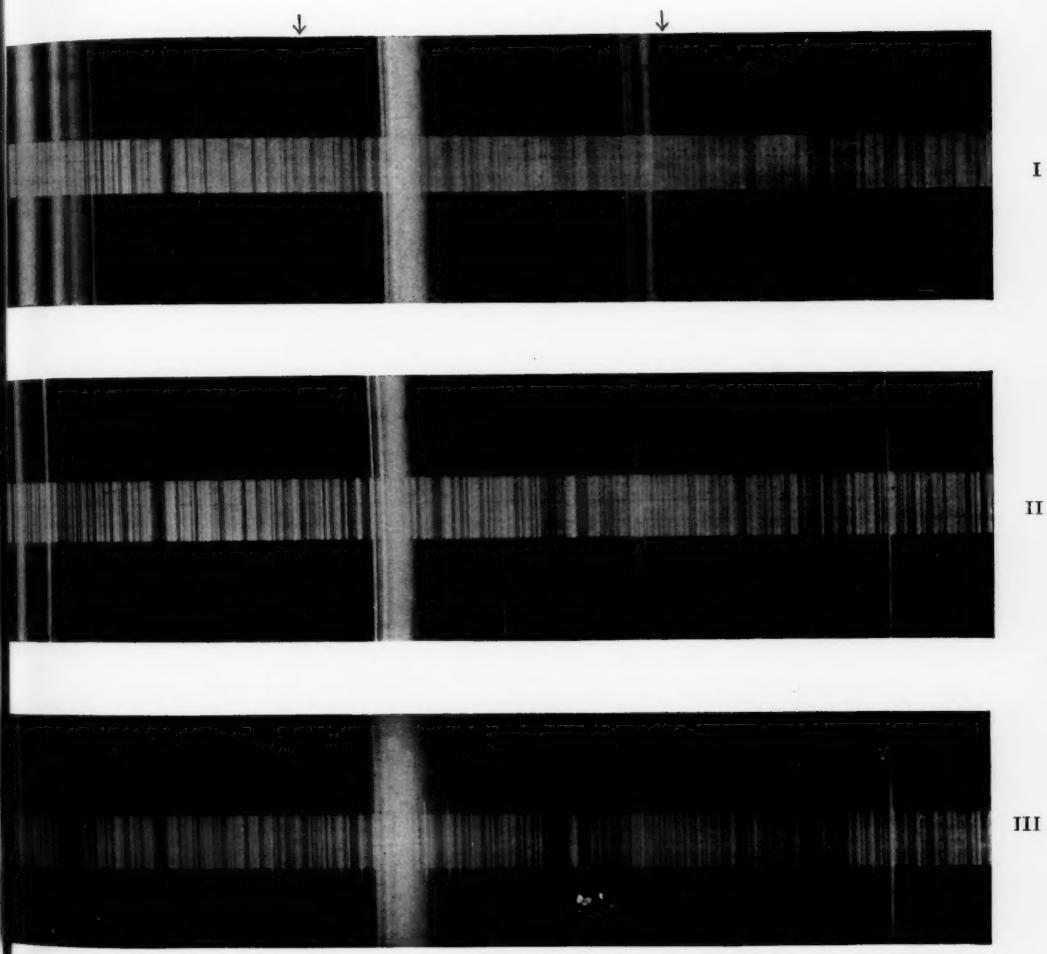
[4] Bonino and Cella, *Atti. Acad. Lincei*, 1931, **13**, 784; also 1932, **15**, 572.

[5] Mukerji, *Phil. Mag.*, 1935, **19**, 1079.

[6] Grassman and Weiler, *Zeit. fur Phys.*, 1933, **86**, 314.



I. Dioxane without filter. II. Dioxane with *o*-cresolthalin filter.
III. Tetralin with *p*-nitrotoluene filter.

THE RAMAN SPECTRUM OF HEAVY WATER.

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1. Introduction.

The Raman spectrum of heavy water was first photographed by Prof. R. W. Wood[1] who used in his investigations two samples of heavy water, one 18% and the other 80%. From his experiments, Wood arrived at the conclusion that the molecules containing one atom of heavy hydrogen (HDO) give a band $\Delta\nu=2623$ cm.$^{-1}$ while those containing two atoms of heavy hydrogen (D_2O) give a band $\Delta\nu=2517$ cm.$^{-1}$; ordinary water gives a band $\Delta\nu=3445$ cm.$^{-1}$ Prof. Wood also remarked in his paper that he was unable to find any structure for these bands. In the case of the vapour, Wood got a line $\Delta\nu=2674$ cm.$^{-1}$ for HDO and $\Delta\nu=2601$ cm.$^{-1}$ for D_2O. Independently of Wood, Rank, Larsen and Bordner[2] photographed the Raman spectrum of heavy water vapour, and they found a line $\Delta\nu=2718$ cm.$^{-1}$ for HDO and $\Delta\nu=2666$ cm.$^{-1}$ for D_2O. Prof. Wood used in his work the resonance line 2536 Å of the mercury arc as the exciting line, while the latter authors used $\lambda=4046$ Å as the exciting line. All the workers complain of the strong fluorescence of the vapour as well as of the liquid, which gave an undesirable background almost blotting out the Raman bands. However, Wood found that the fluorescence of the liquid disappeared after a few hours' exposure to the light of the mercury arc.

Judging from the close similarity in the properties of H_2O and D_2O, it appeared that the results of the above-mentioned authors are necessarily incomplete. The papers on the Raman spectrum of water are legion, and the majority of them seem to agree that the principal band of water consists of three components of which the central one $\Delta\nu=3445$ cm.$^{-1}$ is the strongest. Apart from this a number of low frequency bands of lesser intensity have been noticed in the Raman spectrum of H_2O to which we shall have occasion to refer in the course of the paper. Special mention may, however, be made of the feeble band at 1650 cm.$^{-1}$ which has been observed as a line in the case of the vapour.[3]

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[1] R. W. Wood, *Phys. Rev.*, 1934, **45**, 392.

[2] D. H. Rank, K. D. Larsen and E. R. Bordner, *Jour. Chem. Phys.*, 1934, **2**, 464.

[3] H. L. Johnson and M. K. Walker, *Phys. Rev.*, 1932, **39**, 535.

Theoretically, the computation of the fundamental frequencies of a non-linear triatomic molecule of the type AB_2 has been carried out recently by Van Vleck and Cross,[4] who give for the frequencies of vibration of the H_2O molecule, $\omega_1 = 3520$ cm.$^{-1}$, $\omega_2 = 3560$ cm.$^{-1}$ and $\omega_3 = 1660$ cm.$^{-1}$ Using the same molecular constants, Topley and Eyring[5] find for the frequencies of vibration of the HDO and D_2O molecules the following values :

	ω_1	ω_2	ω_3
HDO ..	3560 cm.$^{-1}$	2600 cm.$^{-1}$	1450 cm.$^{-1}$
D_2O ..	2580 cm.$^{-1}$	2590 cm.$^{-1}$	1250 cm.$^{-1}$

A calculation by Bonner[6] gives for the fundamental frequencies of the H_2O and D_2O molecules respectively

	ω_1	ω_2	ω_3
H_2O ..	3899 cm.$^{-1}$	3807·5 cm.$^{-1}$	1654·5 cm.$^{-1}$
D_2O ..	2865·4 cm.$^{-1}$	2764·7 cm.$^{-1}$	1209·7 cm.$^{-1}$

It might be pointed out that all the three frequencies are active in the Raman effect as well as in the infra-red, although ω_1 is relatively the least active in the Raman effect.

2. Experimental.

In the present work, a sample of 50 grams of 99·2g/100g D_2O ($d^{20}_4 = 1·1049$) supplied by the Norsk Hydro-Elektrisk Kvælstofaktieselskab was employed. The liquid was transferred into a thick-walled pyrex bulb of about 100 c.c. capacity attached to a Wood's tube of about 2 cms. diameter and 15 cms. length. The observation end of the tube was closed by fusing on a flat pyrex window in the usual way. After evacuating the system, the liquid was distilled into the tube and washed back a number of times, till finally the Wood's tube was filled with the dust-free liquid. The tube was suitably painted and illuminated by the light of a quartz mercury lamp concentrated on it by means of a 6-inch condenser. The scattered light was focussed on the slit of a Hilger two-prism spectrograph. When the alignment was perfect, the principal Raman bands could be seen visually with considerable

[4] J. H. Van Vleck and P. C. Cross, *Jour. Chem. Phys.*, 1933, **1**, 350, 357.
[5] B. Topley and H. Eyring, *Jour. Chem. Phys.*, 1934, **2**, 220.
[6] L. G. Bonner, *Phys. Rev.*, 1934, **46**, 458.

brilliancy. Fluorescence was completely absent, and the continuous spectrum practically non-existent. Using Ilford Golden Iso-Zenith plates (H & D 1400), the spectrum could be photographed in all its salient features with an exposure of 10 hours. Longer exposures were tried to detect the presence of fainter bands, if any.

For the sake of comparison the Raman spectrum of ordinary water was also photographed with the same instrument. The water was first purified by distillation from $KMnO_4$ and $Ba(OH)_2$ respectively, and afterwards rendered dust-free by vacuum distillation in the usual way. The Wood's tube, as before, was of pyrex glass with fused-on end-window.

In order to determine the frequency shifts of the Raman bands, an iron arc comparison spectrum was taken in all cases, partially overlapping with the Raman spectrum.

3. *Experimental Results.*

(*a*) *Raman Spectrum of D_2O.*—We shall first consider the Raman spectrum of D_2O. Fig. 2 in the plate shows three broad and intense bands, which are due respectively to the excitation by the 3650 Å, 4046 Å and 4358 Å lines of the mercury arc. Even a casual examination shows that each of these bands consists of three components, of which the component with the largest frequency shift is the faintest. It should, however, be remarked that the 3650 Å excitation really arises from a group of lines all of which are of comparable intensity and hence there is a certain amount of confusion in the corresponding Raman band. Similarly, overlapping occurs between the Raman band excited by the 4046 Å and 4077 Å lines. In order, therefore, to gain a true insight into the structure of the band, we have to confine our attention to the band excited by the 4358 Å line whose companions are relatively very much feebler. The main features of this band are,

(i) it extends roughly over a range of 400 wave numbers ;
(ii) it consists of three distinct components which are fairly but not sharply resolved from one another ;
(iii) the central component is the brightest ; the component with the lowest frequency shift comes next in order of intensity, while the component with the largest frequency shift is comparatively feeble.

The next characteristic feature of the spectrum is the presence of a sharp band shifted by about 1230 cm.$^{-1}$ from the exciting line. This band is very clearly visible in the 4358 as well as in the 4046 excitations. Careful examination of the plate shows a faint companion towards the shorter wavelength side of this band in the 4358 excitation.

Thirdly, the spectrum shows a strong band close to the exciting line, sharp towards the shorter wavelength side, and shading off towards the side of longer wavelength. This band extends from about 130 cm.$^{-1}$ to 240 cm.$^{-1}$ with the intensity maximum at about 175 cm.$^{-1}$

The following table gives the classification of the Raman spectrum of D_2O. The results of other authors are also added for comparison :—

TABLE I.

	Author				Wood	Rank, Larsen & Bordner
Exciting lines	4358	Int.	4046	Int.	2536	4046
Raman lines cm.$^{-1}$	130—240	st.				
	1110	ff.				
	1250	m.	1221	m.		
	2363	st.	2358	st.		
	2515	v.st.	2507	v.st.	2517 (liq.)	
	2662	m.	2680	m.	2601 (vap.)	2666 (vap.)

st.=strong ; v.st.=very strong ; m.=medium ; ff.=very faint.

The above set of measurements were made on one of the best of the author's plates, and are correct to ± 5 wavenumbers. For the frequency shifts of the components of the principal band, the 4358 Å excitation values are probably more accurate, while for the frequency shift of the other band we shall adopt the mean value $\Delta\nu = 1235$ cm.$^{-1}$

(*b*) *Raman Spectrum of H_2O.*—In view of the importance of a comparative study of the Raman spectra of H_2O and D_2O, it may not be out of place to point out the salient features of the Raman spectrum of H_2O. Special mention must be made in this connection to the recent work of Magat[7], Bolla[8], Hulubei[9], Cabannes and De Riols[10] and Ramakrishna Rao[11] on the Raman

[7] M. Magat, *Jour. de Phys.*, 1934, **5**, 346.

[8] G. Bolla, *N. Cimento*, 1932, **9**, 290; *Ibid.*, 1933, **10**, 101.

[9] Hulubei and Cauchois, *C.R.*, 1930, **192**, 1640; *Ibid.*, 1932, **194**, 1475.

[10] Cabannes and De Riols, *C.R.*, 1934, **198**, 30.

[11] I. R. Rao, *Proc. Roy. Soc.*, 1931, **130**, 489; *Ibid.*, 1934, **145**, 489; *Phil. Mag.*, 1934, **17**, 1113.

spectrum of H_2O. While Bolla, Cabannes and De Riols and Ramakrishna Rao claim that the principal band of water consists of three components whose frequency shifts are approximately 3200, 3400 and 3600 cm.$^{-1}$, Magat and Hulubei have not been able to find any trace of the third component with the largest frequency shift. In the Raman spectrum of water taken at room temperature (27° C.) [Fig. 3 in the plate], the author finds that the third component is very faintly present in the Raman band excited by the 4358 Å line of the mercury arc. It is true that this band happens to fall in a region in which the photographic plate is relatively little sensitive, but the time of exposure was adjusted to record it with sufficient intensity. The Raman band due to the 4046 Å excitation also shows a triple structure. The third component is apparently much stronger in this case which is undoubtedly due to the fact that the second component of the band due to the 4077 excitation happens to fall in almost the same position as the third component due to the 4046 excitation.

Besides the principal band, a faint band $\Delta\nu=1650$ cm.$^{-1}$ has been noticed in the Raman spectrum of H_2O by all the above-mentioned authors except Rao. It should be pointed out that the 2536 excitation employed by them is particularly favourable for the observation of this band, since the above band excited by the 4046 Å line chances to fall in the 4358 region and the same due to the 4358 excitation would merge with the principal water band excited by the 4046 Å line. Magat, using a filter which transmits only the 4358 group has, however, been able to record this band. In the photograph reproduced in the plate, this band is faintly visible to the shorter wavelength side of the 4358 group.

Magat has reported a band of medium intensity with $\Delta\nu=5100$ cm.$^{-1}$ However, no trace of this band could be detected in any of the author's plates.

Two other feeble bands with $\Delta\nu=500$ cm.$^{-1}$ and $\Delta\nu=750$ cm.$^{-1}$ have been reported by Magat, Bolla and Cabannes and De Riols. These bands are recorded on the author's plates as a broad structure extending over a region of about 500 wavenumbers.

In addition to these, Bolla and Magat have found a strong band with a frequency shift of about 170 cm.$^{-1}$ In fact the presence of such a strong low frequency band in the case of water was first noticed by Segre.[12] The existence of a similar band in the Raman spectrum of D_2O has been already remarked. This band is also intensely recorded on the author's plates in the case of H_2O. In fact, the 4046 excitation shows a faint but well-defined antistokes for this band.

[12] E. Segre, *Accd. Lincei, Atti.*, 1931, **13**, 929.

The following table gives the frequency shifts of the Raman bands of H_2O. The results of other authors are included for the sake of comparison:

TABLE II.

	Author		Magat		Bolla	Cabannes & De Riols	I. R. Rao
Exciting line	4046	4358	4358	2536	2536	2536	
Raman lines cm.$^{-1}$	134–236(st.)	134–243(st.)	152–225(m.)	175	60(f.) 172(st.)		
	..	464(f.)	600(ff.)	500	510(st.)	550	
	..	754(f.)		740	780(f.)	700	
	1665(f.)	..	1659(f.)	1659 2135	1645(f) 2150(ff.)	1643	
	3231(st.)	3214(st.)	3221(st.)	3200	3200(st.)	3224	3216(st.)
	3436(v.st.)	3428(v.st.)	3435(v.st.)	3400	3435(st.)	3436	3435(v.st.)
	3605(m.)	3600(f.)	..	..	3630(m.)	3625	3528(f.)
					3990(m.)		
			5090(m.)	5100			

st.=strong; v.st.=very strong; m.=medium; f.=feeble; ff.=very feeble.

4. *Discussion of Results.*

(*a*) *Modes of vibration of a non-linear triatomic molecule of the type* AB_2*. —We know that a molecule of this type possesses three fundamental modes of vibration which can be diagrammatically represented as follows:

FIG. 1 (*a*). Normal vibration of H_2O molecule.

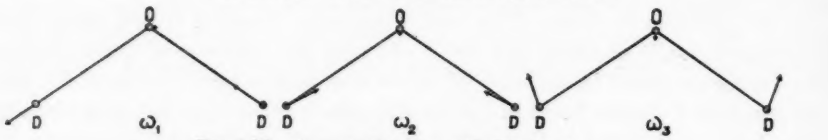

FIG. 1 (*b*). Normal vibrations of D_2O molecule.

* For discussion under this head the author is highly indebted to Mr. N. S. Nagendra Nath, to whom he wishes to acknowledge his thanks.

We may expect ω_2 and ω_3 to be more active in the Raman effect and ω_1 and ω_3 to be more active in the infra-red. In fact, the Raman spectrum of water vapour shows only two frequencies 3655 cm.$^{-1}$ and 1650 cm.$^{-1}$ which may be identified with ω_2 and ω_3 respectively. In the corresponding case of D_2O only one frequency $\Delta\nu=2666$ cm.$^{-1}$ has been so far reported, but the author is quite certain that a careful examination of the Raman spectrum of D_2O vapour will reveal a line at about 1235 cm.$^{-1}$

The infra-red spectrum of heavy water vapour has been studied recently by Bartholomè and Clausius[13] who find the following frequencies :

	ω_1	ω_2	ω_3
H_2O ..	3756	..	1595
HDO ..	3720	2810	1380
D_2O ..	2775	..	1185

ω_2 is observed in the infra-red in the case of HDO, while it fails to appear in the case of the other two symmetrical molecules. The corresponding Raman data are summarised in the table below :

	ω_1	ω_2	ω_3
H_2O ..	..	3655	1650
HDO ..	..	2718 2674	?
D_2O ..	..	2666 2601	(1235)

It is very strange that the value of ω_3 as revealed in Raman spectrum is higher than the observed infra-red value both in the case of H_2O and D_2O.

Adopting the general potential energy function with 4 constants, if we represent the fundamental frequencies of the H_2O molecule by ω_1, ω_2 and ω_3, and those of the D_2O molecule by ω_1^*, ω_2^* and ω_3^* respectively, it can be shown that[14]

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[13] E. Bartholomè and K. Clausius, *Naturwiss.*, 1934, **22**, 420; *Zeit. fur. Elek. Chem.*, 1934, **40**, 530.

[14] See Jenny E. Rosenthal, *Phys. Rev.*, 1934, **45**, 426.

$$\frac{\omega_1}{\omega_1^*} = \left[\frac{D}{H} \cdot \frac{O+2H \sin^2\alpha}{O+2D \sin^2\alpha}\right]^{\frac{1}{2}} \quad .. \quad .. \quad .. \quad (1)$$

and $$\frac{\omega_2\ \omega_3}{\omega_2^*\omega_3^*} = \left[\frac{D^2}{H^2} \cdot \frac{O+2\ H}{O+2\ D}\right]^{\frac{1}{2}} \quad .. \quad .. \quad .. \quad (2)$$

where O, H, D stand respectively for the masses of the oxygen, hydrogen and deuterium atoms, and 2α is the valence angle subtended at the oxygen atom.

In deriving (1) and (2) it is assumed that the valency angle as well as the force constants remain unaltered when one passes from H_2O to D_2O. Bartholomè and Clausius have calculated from equation (1) the vibration frequency of the D_2O molecule assuming the frequency and the valence angle for H_2O, and have found good agreement between the observed and the calculated values. Equation (2), however, affords an independent check on these assumptions purely from Raman data. If we substitute the observed Raman frequencies in the left-hand side of equation (2) we get

$$\frac{\omega_2\ \omega_3}{\omega_2^*\omega_3^*} = \frac{3655 \times 1650}{2666 \times 1235} = 1{\cdot}83$$

The right-hand side of the equation works out as 1·89. The agreement is not unsatisfactory and shows that the force constants and valency angles are nearly but perhaps not quite identical in the two cases.

(*b*) *Structure of the Principal Raman band.*—The structure of the principal Raman band of water does not appear to have been satisfactorily accounted for, although numerous papers have been written over it. The fact that the Raman band of D_2O also shows an exactly identical structure is not surprising in view of the close physical and chemical similarity of these two substances. One important fact that deserves attention is that the frequency of the third component is very nearly identical with the frequency observed in the vapour state, being respectively 3600 and 3655 cm.$^{-1}$ in the case of H_2O and 2662 and 2666 cm.$^{-1}$ respectively in the case of D_2O. In the case of water, Ramakrishna Rao[15] has put forward the theory that there exist three different types of molecules, H_2O, $(H_2O)_2$ and $(H_2O)_3$. Rao attributes the component of highest frequency observed in the Raman spectrum of water to the H_2O molecules, while the components of lower frequency are attributed respectively to the $(H_2O)_2$ and $(H_2O)_3$ molecules. Rao gives the following arguments in favour of his theory :

(i) the frequency of the third component of the Raman band is not very different from the frequency observed in the vapour state;

(ii) as the temperature of water is raised the third component goes on gaining in intensity, while the first one goes on diminishing

[15] I. R. Rao, *loc. cit.*

in intensity ; this is in all probability due to the breaking up of the higher polymers, evidence of whose existence in water is available from entirely different sources ;

(iii) the Raman spectrum of ice shows only the first two components, which are sharper than in the case of water and are shifted slightly towards the exciting line. This is because all the water molecules exist as double and triple molecules in the case of ice ;

(iv) the Raman spectrum of crystals containing water of crystallisation shows only the first or the first two components, but in no case the third.

Although the reasoning appears quite plausible, Sutherland[16] has pointed out that the assumption of the existence of triple molecules in water and ice is contrary to experimental evidence. He finds that the character of the Raman spectrum of ice taken at liquid air temperature is strikingly different from that taken at 0° C. The component of lowest frequency is much sharper and stronger at the lower temperature, which is explicable on Rao's theory only if we make the improbable assumption that even in the crystalline state a gradual polymerisation into $(H_2O)_3$ molecules takes place. X-ray observations[17] do not however show any change in the crystal structure of ice between 0° C. and −183° C. Sutherland attributes the component of frequency 3200 cm.$^{-1}$ to $(H_2O)_2$ molecules, and postulates that the other two frequencies arise because of a doubling of the H_2O frequency from a condition of resonance degeneracy such as has been observed in the case of CO_2. "This is suggested by the fact that one of the other fundamental frequencies of water is known from infra-red and Raman spectra to lie near 1650 cm.$^{-1}$ so that its first overtone may fall close enough to the fundamental for these two levels to interact. As the temperature is lowered the position of the fundamental shifts considerably, as well as being more sharply defined, so that the interaction between the two levels may become negligible and only one frequency will be observed."

The explanation of Sutherland, however, appears rather far-fetched. The analogy with CO_2 appears difficult to understand. It need only be pointed out that whereas the frequencies 1285 and 1388 cm.$^{-1}$ of the components into which the fundamental frequency is split up in the case of CO_2 lie one on either side of the octave of the other fundamental frequency 668 cm.$^{-1}$, the author is unable to find any such relation in the case of either H_2O or D_2O. The investigation of the band structure of HDO would be of great interest in this connection.

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[16] G. B. B. M. Sutherland, *Proc. Roy. Soc.*, 1933, **141**, 542.

[17] See Barnes, *Proc. Roy. Soc.*, 1929, **125**, 670.

Recently Bernal and Fowler[18] have proposed a model of the water molecule from considerations of spectral and X-ray data, which has proved to be of great help in explaining either quantitatively or qualitatively several properties of water and ionic solutions. According to this model an H_2O molecule of radius 1·4 Å is surrounded by four others in a more or less regular tetrahedron. "This is the arrangement found in ice and necessarily follows from the quasi-tetrahedral angle of the H_2O molecule." As regards the arrangement of the molecules of H_2O in water, Bernal and Fowler postulate three chief forms of arrangement :—"Water I, tridymite-ice-like, rather rare, present to a certain degree at low temperatures below 4° C.; water II, quartz-like predominating at ordinary temperatures; water III, close-packed ideal liquid, ammonia-like predominating at high temperatures for some distance below the critical point at 374° C. These forms pass continuously into each other with change of temperature..... The sequence water I–II–III is one of increasing rotatory and translatory molecular movement and of the consequent diminution of the dipole forces of cohesion of the liquid and relative increase of the Van der Waals component..... It is tempting to identify the 3200, 3400, 3600 (Raman) bands as corresponding respectively to the water structures I, II and III, but such a correspondence cannot be maintained until the nature of the transitions corresponding to these bands has been worked out."

We may here point out one significant fact of experimental observation, that while the frequency difference of the components of the band is about 200 cm.$^{-1}$ in the case of H_2O, this difference is only about 150 cm.$^{-1}$ in the case of D_2O.

(*c*) *Band* $\Delta\nu = 500$ *cm.*$^{-1}$—This diffuse band has been attributed by Magat to the frequency of hindered rotation or oscillation of the water molecules. However, this assignment would appear to be purely conjectural, and the origin of this band as well as of the band $\Delta\nu = 750$ cm.$^{-1}$ remains rather obscure. It is surprising that while Magat[19] has found that these bands disappear at about 40° C., Bolla[20] has quite recently reported that these bands persist in the Raman spectrum of water at all temperatures from 28° to 92°C.

(*d*) *Band* $\Delta\nu = 175$ *cm.*$^{-1}$—Segre who was the first to observe this strong band in the case of H_2O suggested that it might be due to the oscillation in the polymers of H_2O. He found that raising the temperature, which tends to reduce the number of associated molecules, decreased the intensity

[18] Bernal and Fowler, *Jour. Chem. Phys.*, 1933, **1**, 515.
[19] M. Magat, *Jour. de Phys.*, 1934, **5**, 347.
[20] G. Bolla, *N. Cimento*, 1935, **12**, 243.

of this band. Magat has made an attempt to calculate the frequency of such an oscillation on the approximate assumption that it is analogous to the intramolecular vibration of a diatomic molecule, and employing the empirical formula of Morse[21] connecting the frequency ω_0 and the internuclear distance r_0

$$\omega_0 r_0^3 = 3000 \text{ Å}^3/\text{cm}.$$

Putting $r_0 = 2{\cdot}72$ Å (diameter of the H_2O molecule), we get $\omega_0 = 150$ cm.$^{-1}$ In view of the highly empirical nature of the procedure, the agreement seems satisfactory.

Alternatively, Magat has calculated the frequency of such an intermolecular vibration as 200 cm.$^{-1}$ by employing the model proposed by Bernal and Fowler, which value again falls in the observed range. However, as Magat himself has remarked, such a vibration cannot appear in the infra-red, since the total electric moment of a group of five molecules would on the average be zero.

The existence of a strong infra-red absorption for water at about 160 cm.$^{-1}$ has been found recently by Cartwright.[22] In a later note in *Nature*,[23] Cartwright has reported that D_2O also shows a strong infra-red absorption in practically the same region. These results fit in very well with the author's observation that the corresponding Raman band in the case of H_2O and D_2O are practically in the same position. Cartwright originally attributed the infra-red band in the case of H_2O to a hindered rotation of the water molecules. Support for the view that the molecules in a liquid exist in a quasi-crystalline state is forthcoming from divers sources. Recently Debye[24] has adduced strong evidence to show that the rotation of the dipole through 90°C. in the case of H_2O would produce a potential energy of about $10\,kT$. If we adopt this value and calculate the frequency of hindered rotation about the axis perpendicular to the plane of the molecule (assuming the oscillation to be approximately harmonic), we get a value of 200 cm.$^{-1}$

However, such a simple calculation leaves unexplained the observed fact that the frequency of the band is practically the same in the case of H_2O and D_2O. If the origin of the band is to be sought for in the rotation of the individual dipoles, it follows that the frequency of the band ought to be affected by a factor $\sqrt{2}$ when we pass from H_2O to D_2O. Cartwright has therefore modified his original statement, and has attributed the infra-red

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[21] P. M. Morse, *Phys. Rev.*, 1929, **34**, 57.

[22] C. H. Cartwright, *Nature*, 1935, **135**, 872.

[23] C. H. Cartwright, *Nature*, 1935, **136**, 181.

[24] P. Debye, *Phys. Zeit.*, 1935, **36**, 100, 193.

absorption band at 160 cm.$^{-1}$ to the hindered translation of the liquid molecules, in which case the change in frequency from H_2O to D_2O would be small, in conformity with the experimental result. We may point out that the difficulty of attributing the band to hindered rotation of the molecules might be overcome, if it be assumed that the rotating entities are not the individual molecules, but the polymers of H_2O and D_2O respectively. The knowledge of the state of polarisation of the band would most probably throw light on its origin ; measurements are now on hand for this purpose.

In conclusion, the author wishes to record his respectful thanks to Professor Sir C. V. Raman for his kind interest and helpful guidance in the course of the present investigation.

5. *Summary.*

The Raman spectrum of heavy water (D_2O) photographed with a Hilger two-prism spectrograph shows a strong band with three imperfectly resolved components whose frequency shifts are 2363, 2515 and 2662 cm.$^{-1}$ Besides, a sharp band with a frequency shift of 1235 cm.$^{-1}$ with a feeble companion at about 1110 cm.$^{-1}$ has been recorded, and a strong low frequency band $\Delta\nu = 175$ cm.$^{-1}$ The triple structure of the principal band as well as the existence of the other two bands has been noticed for the first time. A comparative study of the Raman spectra of H_2O and D_2O has been made and many points of similarity noticed. Purely from Raman data, it is shown that the valency angles and force constants do not alter much as one passes from H_2O to D_2O. It is pointed out that the triple structure of the principal band is probably due to the fact heavy water is also polymerised similar to H_2O. The low frequency band appears to be intimately connected with the nature of the liquid state.

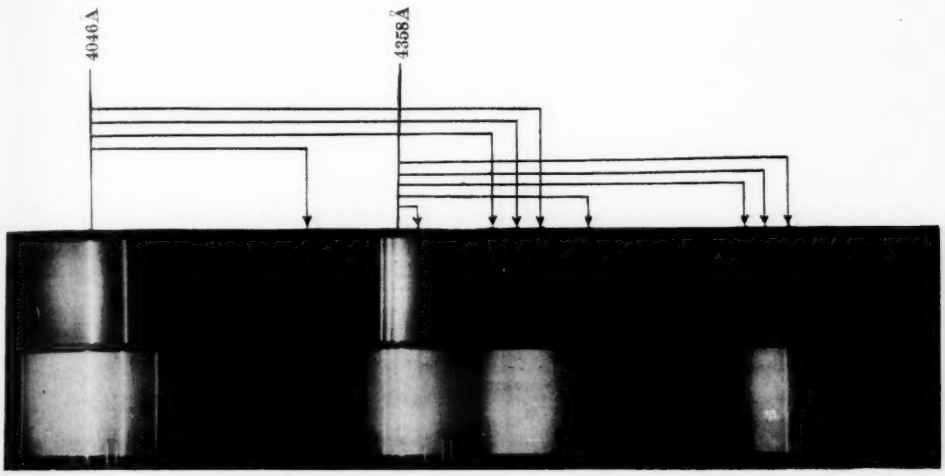

FIG. 2. Raman Spectrum of D_2O.

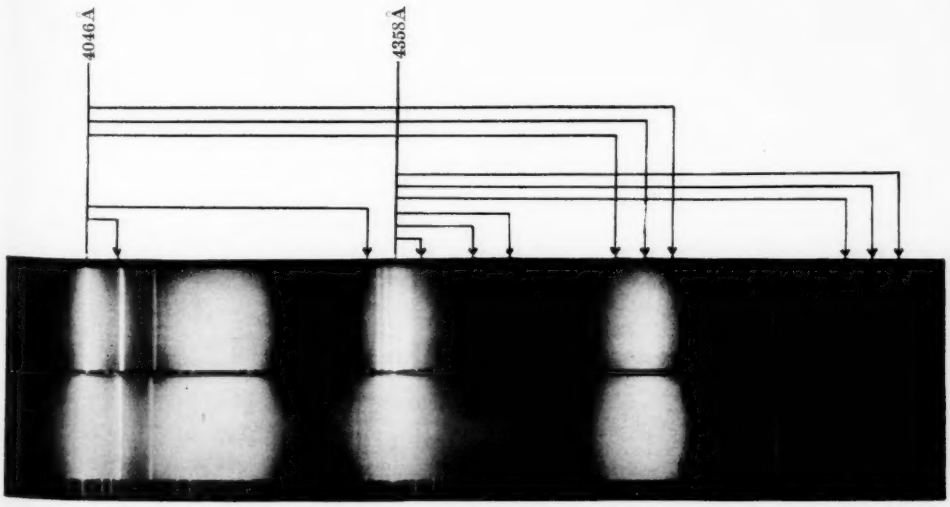

FIG. 3. Raman Spectrum of H_2O.

RAMAN SPECTRUM OF DEUTERIUM : I.

By S. Bhagavantam.

(*From the Department of Physics, Andhra University, Waltair.*)

Received September 3, 1935.

1. *Introduction.*

In two earlier papers (Bhagavantam, 1932), the author studied the Raman spectrum of ordinary hydrogen in all its aspects in great detail using a specially constructed high pressure gas tube as the container for the gas. It is felt that these investigations should be extended to the case of heavy hydrogen as of all the other molecules that are amenable to such studies, it comes next in simplicity. The necessity of making a complete experimental survey of the Raman spectrum in such a case so as to include all the important features such as the intensity relationships, polarisation characters and fine structure of the lines, need not be overstressed here. It may, however, be pointed out that ordinary and heavy hydrogen constitute the only two cases which may be expected to furnish unique experimental evidence on a variety of points in favour or otherwise of the existing theories of the Raman effect. This, of course, is intimately connected with the very low moments of inertia and the simplicity of structure of these molecules. The present paper is the first of a series dealing with the Raman spectrum of deuterium which the author proposes to publish and contains the preliminary results obtained in this direction.

2. *Experimental.*

Preparation of Deuterium.—The following procedure is adopted for preparing deuterium under high pressure. About 5 grammes of heavy water supplied as 99·5% pure by the Ohio Chemical and Manufacturing Company is further purified by slow distillation in an evacuated and sealed double bulb of pyrex glass. The water thus purified is transferred to a thin wall glass capsule. The glass capsule is sealed off and carefully inserted into a specially prepared steel bomb. About 6 grammes of sodium and a small steel hammer are introduced into the bomb which is then closed. Through a pin valve connected to the bomb all the enclosed air is removed thoroughly by means of an efficient oil pump, till a manometer connected in the circuit showed that any air that may have been left inside the bomb is only at a pressure of a fraction of a millimeter. The pin valve is then closed and the

steel hammer dropped, by suitably tilting the bomb, on to the water bulb. The bulb breaks and the water at once reacts with the sodium thus generating deuterium inside the bomb at a high pressure. The volume chosen for the bomb is such that the above quantities of heavy water and sodium have generated a pressure of about 100 atmospheres. The reaction is almost instantaneous and is accompanied by the evolution of a large quantity of heat. The total volume of the deuterium generated is about 3 litres at atmospheric pressure.

The gas is then allowed to cool and is transferred into the experimental tube designed for a study of the Raman effect in gases at high pressures and described by the author in the earlier papers already referred to. The connecting tubes used in transferring the gas and the experimental tube are thoroughly evacuated beforehand through pin valves. In this way the experimental tube is filled with fairly pure (nearly 100%) deuterium at a pressure of about 17 atmospheres.

Exposure.—Light from a six-inch quartz mercury arc is condensed by means of a large glass condenser on to the gas tube. The scattered light is focussed with a short focus lens on the slit of a Hilger 2 prism glass spectrograph of high light gathering power. Using a slit width of 0·05 mm. a continuous exposure of about 72 hours is found necessary to record the Raman spectrum with reasonable intensity. Golden Isozenith plates have been used for photographing the spectra.

3. Results.

Table I gives the various lines recorded and measured in the Raman spectrum of deuterium in the present investigation. The plate shows other feeble lines which are not included in the table and these will be measured and interpreted in subsequent communications after obtaining more intense photographs. Figs. (*a*) and (*b*) in the Plates are respectively the Raman spectrum of deuterium and a microphotometric record of the same. The transitions are given for some of the rotation lines that are easily seen in the reproductions. V.R. indicates the vibration Raman line excited by λ 4046. The microphotometric record is confined only to the rotation lines in the neighbourhood of λ 4358 and is intended to exhibit the approximate relative intensities of these lines. The most remarkable feature s the alternation of intensities, lines representing transitions between even rotational quantum numbers being stronger than those that represent transitions between odd rotational quantum numbers. The nearly equal intensity of the $0 \rightarrow 2$ and the $2 \rightarrow 4$ lines may also be noted and is of special significance.

TABLE I.

Raman Spectrum of Deuterium.

Wave-length	Approx. Rel. Intensity	Exciting line	Frequency shift	Quantum transition	
				J	n
4604·27	2	4046	2992·7	$\left\{\begin{matrix}0\to0\\1\to1\\\text{etc.}\end{matrix}\right\}$	0→1
4484·13	1	4358	643·5	4 → 6	
4461·58	1	,,	530·8	3 → 5	
4438·69	5	,,	415·2	2 → 4	
4415·58	3	,,	297·4	1 → 3	
4392·74	5	,,	179·5	0 → 2	
4324·77	0	,,	−178·1	2 → 0	
4302·54	0	,,	−297·5	3 → 1	
4115·67	4	4046	414·9	2 → 4	
4096·02	3	,,	298·4	1 → 3	
4018·01	0	,,	−175·4	2 → 0	

4. Discussion of Results and their Comparison with Theory.

(*a*) *Frequency Shifts and the Molecular Constants.*—The Raman spectrum of deuterium at a pressure of 2·5 atmospheres has been investigated by Anderson and Yost (1935) recently using λ 2537 of mercury as the exciting radiation. These authors have reported two rotation lines having frequency shifts of 179·6 and 298·3 and a vibration line having a frequency shift of 2989·5. These figures are in satisfactory agreement with those obtained by the author. In the present investigation use is made of λ 4358 as the exciting radiation and it has been possible to record several other rotation lines and some antistokes lines as the gas is obtained at a much greater pressure. Hitherto there existed no direct experimental evidence for the molecular constants of deuterium. These have been derived by Urey and Teal (1935) only indirectly by making use of the data available for the H_2 and HD molecules with the help of the usual relations between the constants of

isotopic molecules. Anderson and Yost have shown that these constants satisfactorily predict the positions of the two rotation lines observed by them in the Raman spectrum of deuterium. This agreement may be regarded as the first direct experimental evidence for the molecular constants of deuterium but cannot be considered complete as the anharmonic constants and the small correction terms do not make themselves felt appreciably until we reach large rotation quantum numbers. The fact that in the present investigation, five lines have been recorded and measured, enables us to make the comparison much more complete and the results provide a most satisfactory confirmation of the constants derived by Urey and Teal. The rotational energy of a diatomic molecule in a specified electronic state and zero vibrational state is given by the following equation

$$\frac{E_J}{hc}=\left[B_e-\frac{\alpha_e}{2}+\frac{\gamma}{4}-\frac{\delta}{8}\right]J(J+1)+\left[D_e+\frac{\beta}{2}\right]J^2(J+1)^2+F_eJ^3(J+1)^3 \quad .. \quad (1)$$

In this equation J is the rotational quantum number and B_e is the moment of inertia of the molecule in a state of vibration of infinitesimal amplitude and is related to B_o the moment of inertia of the molecule in the zero vibrational state by the equation

$$B_o=B_e-\frac{\alpha_e}{2}+\frac{\gamma}{4} \text{ etc.} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad (2)$$

The other constants are all small and enter only as correction terms. Assuming, in accordance with Urey and Teal, that $B_e=30\cdot459$; $\alpha_e=1\cdot0858$; $\gamma=0\cdot01713$; $\delta=0\cdot00115$; $-D_e=0\cdot01121$; $\beta=2\cdot39\times10^{-4}$, the rotational energies pertaining to the various J values are calculated from (1) and the frequency shifts of the Raman lines $0\rightarrow2$, $1\rightarrow3$, etc. are deduced. These are given in Table II along with the frequency shifts observed in the present investigation for comparison. Since the antistokes rotation lines and those excited by λ 4046 are somewhat weak, in giving the figures in Table II, only the lines excited by λ 4358 are taken into consideration.

TABLE II.

Comparison with Theory.

Transition	J : $0\rightarrow2$	$1\rightarrow3$	$2\rightarrow4$	$3\rightarrow5$	$4\rightarrow6$
Observed frequency	179·5	297·4	415·2	530·8	643·5
Calculated frequency	179·1	297·7	414·9	530·3	643·5
	-.4	+.3	-.3	-.5	0

The excellent agreement between the two sets of values up to the fifth rotation line must be regarded as a satisfactory confirmation of both the main molecular constants and the correction terms as well.

(*b*) *Relative Intensities of the Rotation Lines, Spins and Statistics of the Nuclei.*—From observations on the alternation of intensities in the *a* bands of deuterium, Lewis and Ashley (1933) have concluded that the nucleus of deuterium obeys the Einstein-Bose statistics, and that the spin cannot be zero. Murphy and Johnston (1934) working on the Fulcher spectrum of D_2 have concluded that the statistical weight of the symmetric states is twice that of the antisymmetric states. This would mean that the spin of the deuterium nucleus is 1. These results indicate that in the Raman spectrum of deuterium, unlike the case of ordinary hydrogen whose nuclei obey the Fermi-Dirac statistics, the lines representing transitions between even rotational quantum numbers should be stronger than those that correspond to transitions between odd rotational quantum numbers. This is most satisfactorily confirmed in the present investigation as may be seen from Figs. (*a*) and (*b*) in the Plates. The formulæ originally developed by Manneback (1930) and subsequently also given by Placzek (1934) for the relative intensities of the rotational Raman lines in the case of a diatomic molecule are made use of in calculating the intensities given in Table III. It is assumed that molecules with even rotational quantum numbers have a statistical weight twice as large as that possessed by those having odd rotational quantum numbers. The calculations are for a temperature of 30° C. and assume that $B_0 = 29 \cdot 916$.

TABLE III.

Calculated Relative Intensities of the Rotation Lines.

P P Series: $J \rightarrow J-2$.		R R Series: $J \rightarrow J+2$	
Transition	Intensity	Transition	Intensity
2→0	0·571	0→2	1·333
3→1	0·220	1→3	0·904
4→2	0·202	2→4	1·467
		3→5	0·407
		4→6	0·322
		5→7	0·020

The figures are only relative and have no absolute significance. It is easily seen from the pictures that the relative intensities experimentally obtained are in qualitative agreement with the above figures. The fact that the lines $0 \rightarrow 2$ and $2 \rightarrow 4$ are to be expected to be of nearly the same intensity, both being more intense than $1 \rightarrow 3$ is beautifully confirmed in the microphotometric record of Fig. (*b*) in the Plates. The intensity distribution amongst the various lines is a very exceptional one and has not been observed in any of the Raman spectra so far studied.

(*c*) *The Vibration Line and Its Fine Structure.*—The vibration line $n : 0 \rightarrow 1$ should consist of several fine structure components arising from different molecules belonging to different rotational states. The spacing of these may be calculated using the constants given by Urey and Teal. In the present investigation, however, the resolution employed and the exposure given are sufficient only to bring out the strongest of these components and a detailed calculation of the positions and the relative intensities of these components is therefore postponed to a later communication. The strongest line should have a frequency shift of 2991·2* and the observed value of 2992·7 is in good agreement with this figure. Anderson and Yost have given 2989·5 for the frequency shift of this line.

5. *Summary and Conclusion.*

The paper describes the results of a study of the Raman spectrum of deuterium at a pressure of about 17 atmospheres using λ 4358 of mercury as the incident radiation.

Rotation lines having frequency shifts $\pm 179 \cdot 5$, $\pm 297 \cdot 4$, 415·2, 530·8 and 643·5 and a vibration line with a shift of 2992·7 have been observed. These shifts are in excellent agreement with and provide for the first time a direct experimental confirmation of the molecular constants given by Urey and Teal for the D_2 molecule.

The relative intensities of the rotation lines are in agreement with the fact that the deuterium nucleus has a spin of one unit and obeys the Bose-Einstein statistics. States characterised by even rotational quantum numbers are given a statistical weight twice as large as that of those having odd rotational quantum numbers.

The intensity distribution is in qualitative agreement with that predicted by the theory developed by Manneback for the rotational Raman scattering in diatomic molecules.

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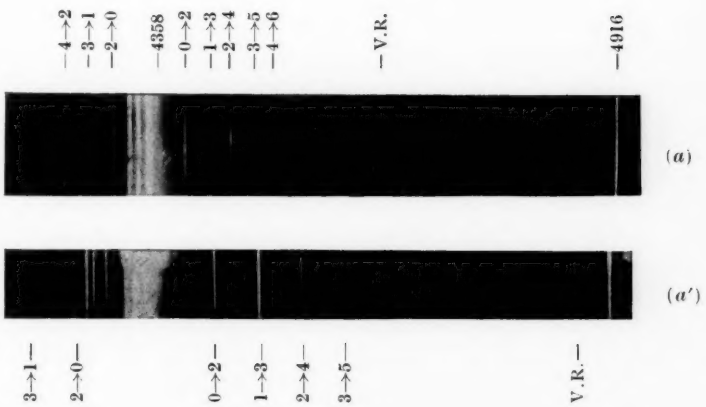
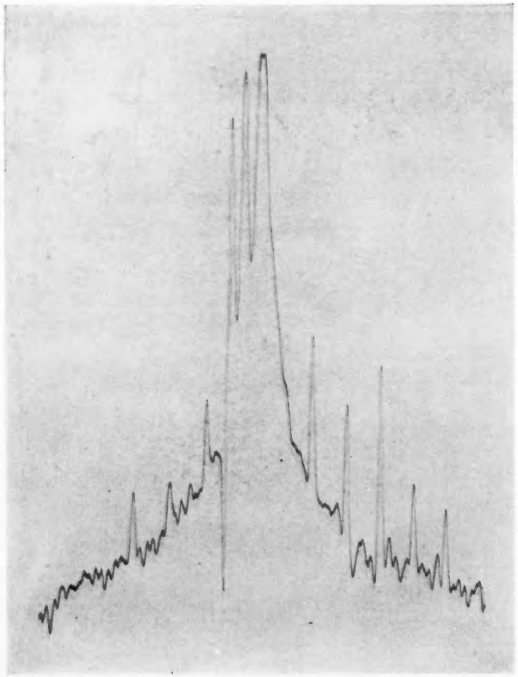
* See T. F. Anderson and D. M. Yost, *loc. cit.*

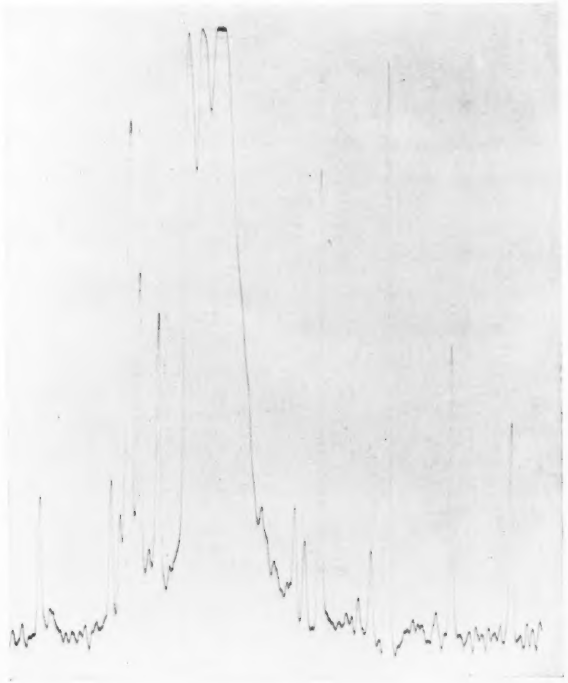


(*a*) Raman Spectrum of Deuterium.
(*a′*) Raman Spectrum of Hydrogen on the same scale for comparison.



(*b*)

(*b*) Microphotometric record of the Raman Spectrum of Deuterium.



(*b'*)

(*b'*) Microphotometric record of the Raman Spectrum of Hydrogen on the same scale.

A more detailed and quantitative investigation of the intensity, fine structure and polarisation characters is in progress and will form the subject-matter of a further communication.

In conclusion, the author desires to express his grateful thanks to Sir C. V. Raman for his kind encouragement and a loan of the heavy water used in the present investigation.

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T. F. Anderson and D. M. Yost	*Jour. Chem. Phys.*, 1935, **3**, 242.
S. Bhagavantam	*Ind. Jour. Phys.*, 1932, **7**, 107 and 549.
G. N. Lewis and M. F. Ashley	*Phys. Rev.*, 1933, **43**, 837.
C. Manneback	*Z. f. Phys.*, 1930, **62**, 224; and **65**, 574.
G. M. Murphy and H. Johnston	*Phys. Rev.*, 1934, **45**, 500 and 761; and **46**, 95.
G. Placzek	*Handbuch Der Radiologie*, 1934, **6**, Part 2, 205.
H. C. Urey and G. K. Teal ..	*Rev. Mod. Phys.*, 1935, **7**, 34.

RAMAN SPECTRUM OF HYDROGEN DEUTERIDE.

By S. Bhagavantam.

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Received September 13, 1935.

1. Introduction.

In an earlier paper in this Journal* the author had described the results of a study of the Raman spectrum of deuterium. Subsequent to this, a particularly intense picture of the scattered spectrum is obtained using the same sample of the gas as in the previous investigation with a view to complete the work in all its aspects. This photograph, besides showing the Raman lines of D_2 very intensely, is found to exhibit another feeble series of lines excited by λ 4358. Measurement revealed that these have their origin in the HD molecules. The extreme feebleness of the lines in comparison with the D_2 lines indicates that the HD molecules are present in a very small proportion in the sample under investigation. A search is made for the well-known Raman lines of the H_2 molecule but none has been found. It may, therefore, be concluded that the sample contains no appreciable proportion of H_2 molecules. In the present paper the results of the measurements relating to the HD series of Raman lines are given.

2. Results.

Table I.

Raman Spectrum of Hydrogen Deuteride.

Wave-length	Exciting line	Approx. rel. intensity	Frequency observed	Frequency calculated	Transition J→J′
4479·0	4358	0	618	614·8	2 → 4
4443·9	,,	½	442	442·1	1 → 3
4409·6	,,	0	267	266·5	0 → 2
4308·7	,,	0	−264	,,	2 → 0

The lines having frequency shift of 442 is the strongest of the series and the corresponding line excited by λ 4046 is also seen and measured on the plate.

* See page 303 of this number.

3. *Discussion of Results.*

Jeppesen[1] (1934) and Beutler and Mie[2] (1934) have analysed the bands due to the HD molecule in the ultra-violet. Urey and Teal[3] (1935) have recently given the following constants for the normal state of this molecule in order to account for the experimental data of the above authors.

$$B_e=45\cdot6549\,;\ \alpha=1\cdot9928\,;\ \gamma=0\cdot03850\,;\ \delta=0\cdot00317\,;\ -D_e=0\cdot02602\,;$$
$$\beta=6\cdot58\times10^{-4}\,;\ F_e=2\cdot19\times10^{-5}.$$

These constants are used in calculating the frequencies of the various rotation Raman lines $0\rightarrow2$, $1\rightarrow3$ and $2\rightarrow4$ as in the foregoing paper and the results are given in Table I for comparison. The agreement between the observed and calculated frequency shifts is very satisfactory in view of the extreme feebleness of the lines.

Another outstanding feature of the spectrum is the absence of the phenomenon of alternating intensities. The intensity rises to a maximum at the second rotation line corresponding to $1\rightarrow3$† and then falls off. This is in accordance with what may be expected as the molecule is composed of unlike nuclei. The relative intensities of the rotation lines that are to be expected on the basis of Manneback's expressions (Manneback,[4] 1930) are calculated and given in Table II. Same statistical weight is assigned to

TABLE II.

Calculated Relative Intensities of the Rotation Lines.

PP Series J→J−2		RR Series J→J+2	
Transition	Intensity	Transition	Intensity
2 → 0	0·188	0 → 2	0·666
3 → 1	0·095	1 → 3	0·786
		2 → 4	0·483
		3 → 5	0·176
		4 → 6	0·040

[1] C. R. Jeppesen, *Phys. Rev.*, 1934, **45**, 480.
[2] H. Beutler and K. Mie, *Naturwiss.*, 1934, **22**, 418, and subsequent papers.
[3] H. C. Urey and G. K. Teal, *Rev. Mod. Phys.*, 1935, **7**, 34.
† It may be noted that in D_2, this line is weaker than the first rotation line $0\rightarrow2$.
[4] C. Manneback, *Z. f. Phys.*, 1930, **62**, 224; and **65**, 574.

both even and odd rotational states. The calculations are for a temperature of 30°C. and the value of B_0 is taken as 44·67.

The fact that the intensity reaches a maximum at the second line and then falls off is nicely confirmed. A more detailed comparison is not at present possible owing to the feebleness of the lines. The stokes lines represented by $3 \rightarrow 5$ and $4 \rightarrow 6$ and the antistokes line $3 \rightarrow 1$ have not been recorded.

In conclusion the author desires to express his grateful thanks to Sir C. V. Raman for his kind interest in the work.

4. *Summary.*

Using λ4358 as the exciting radiation, frequency shifts of 267, 442 and 618 arising respectively from the rotational transitions $0 \rightarrow 2$, $1 \rightarrow 3$ and $2 \rightarrow 4$ have been recorded in the Raman spectrum of hydrogen deuteride gas. The figures compare well with 266·5, 442·1 and 614·8 which are calculated on the basis of the molecular constants given by Urey and Teal for the HD molecule. The antistokes line arising from the transition $2 \rightarrow 0$ is also recorded. The phenomenon of alternating intensities is not observed and the line corresponding to $1 \rightarrow 3$ is the most intense one in the series as may be expected.

HYPERFINE STRUCTURE IN SELENIUM, PALLADIUM AND GOLD.*

By L. Sibaiya.

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Received September 10, 1935.

Selenium (At. no. 34; At. wt. 79·2).

For purposes of classification of selenium spectra, the arc and spark lines of selenium have been mostly excited in tubes of various types with condensed or uncondensed electrical discharge through selenium vapour or between aluminium poles tipped with metallic selenium. A selenium arc either in vacuum or in an atmosphere of nitrogen has also been employed. Such sources however are not suited for hyperfine structure work, as the lines obtained are broad and diffuse. Moreover most of the prominent arc lines of selenium lie either in the near infra-red or in the extreme ultra-violet, thus rendering their analysis by high resolving power apparatus specially difficult. Some intense spark lines of selenium lie in the visible region; but under the conditions employed for their emission in discharge tubes, the broadening of the lines renders such sources unsuitable for hyperfine structure study. The apparatus used, the essential part of which is a water-cooled hollow cathode, is the same as that employed by Prof. Venkatesachar and the author in their investigation on the isotopic constitution of platinum.[1] The selenium powder took the place of the platinum foil in the tubular space of the cathode (Pl. XV, Fig. 1). For experimental details the above paper must be consulted.

Of the seventeen lines of selenium here examined, only two are arc lines and the remaining fifteen belong to the first spark spectrum of selenium.

Se I lines.

λ in Å.U.	Classification
4739·03	$5s(^4S)\ ^5S_2—6p(^4S)\ ^5P_2$
4730·79	$5s(^4S)\ ^5S_2—6p(^4S)\ ^5P_3$

* An oral communication of the main results contained in this paper was made at the Meeting of the Academy on 19th June 1935.

[1] Venkatesachar and Sibaiya, *Proc. Ind. Acad. Sci.*, 1935, **1**, 955.

The spectral classification of the arc lines is taken from Meissner, Bartelt and Eckstein.[2]

The spark lines here analysed are listed below ; they have been classified differently by Bartelt[3] and Krishnamurthy and Rao[4]:

Se II LINES (λ in Å.U.).

5305·41	5143·15	4840·61
5253·69	5068·67	4763·66
5253·13	4992·88	4648·40
5227·53	4975·76	4618·75
5175·97	4844·98	4602·32

All the above Se I and Se II lines are sharp and single (Pl. XV, Fig. 2). Selenium, according to Aston, has the following isotopic constitution:

Mass number	74	76	77	78	80	82
Percentage abundance ..	0·9	9·5	8·3	24·0	48·0	9·3

The even isotopes of selenium amount to 91·7% ; the single odd isotope Se 77 is present only to the extent of 8·3%. It is therefore difficult to observe the components arising from a splitting of the gross multiplet levels due to a nuclear spin in Se 77. In each of the lines examined the observed component is to be ascribed to the even isotopes whose total abundance is 91·7%. Even isotope displacement, if any, could have been detected because Se 80 (48%) is twice as abundant as Se 78 (24%), the other two Se 76 and Se 82 being nearly equally abundant (9·4%). The absence of structure revealed by the lines indicates that none of the levels here observed shows any even isotope displacement and that all the even isotopes of selenium have nuclear spins equal to 0. From an examination of two lines in the arc spectrum of selenium Rafalowski[5] has come to the same conclusion. Though the absence of structure leads to the conclusion that the nuclear magnetic moment of Se 77 is small, there is however a faint component ($\sim +0{\cdot}093$ cm.$^{-1}$?) that accompanies 5227·53 Å, a fact which can be most simply explained by ascribing a nuclear spin of $\frac{1}{2}\frac{h}{2\pi}$ to the odd isotope 77.

[2] Meissner, etc., *Zeits. f. Physik*, 1934, **91**, 432.
[3] Bartelt, *Zeits. f. Physik*, 1934, **91**, 450.
[4] Krishnamurthy and Rao, *Proc. Roy. Soc.*, 1935, **149**, 56.
[5] Rafalowski, *Acta Physica Polonica*, 1933, **2**, 119.

Palladium (At. no. 46 ; At. wt. 106·7).

Since the isotopic constitution of palladium by the mass-spectrograph method has not been found,† the hyperfine structure of the palladium lines is here studied with the object of determining, if possible, the isotopes of palladium. A thin palladium foil‡ is introduced into the hollow cathode, which is excited by a D. C. 1 kilowatt generator with a discharge current of 200 mA at 1700 v. The following arc lines were analysed ; the classification of the lines is taken from Shenstone[6]:

Pd I LINES.

λ in Å.U.	Classification	
3242·72	$5s\ {}^3D_3$—$5p\ {}^3D^o_3$	
3251·66	$5s\ {}^3D_1$—$5p\ {}^1P^o_1$	
3302·15	$5s\ {}^3D_1$—$5p\ {}^3D^o_1$	
3404·60	$5s\ {}^3D_3$—$5p\ {}^3F^o_4$	
3421·24	$5s\ {}^3D_2$—$5p\ {}^3D^o_2$	
3433·44	$5s\ {}^1D_2$—$5p\ {}^1P^o_1$	
3441·40	$5s\ {}^1D_2$—$5p\ {}^1D^o_2$	*Vide* Pl. XVI, Fig. 3.
3460·76	$5s\ {}^3D_3$—$5p\ {}^3F^o_3$	
3481·17	$5s\ {}^3D_1$—$5p\ {}^3F^o_2$	
3489·79	$5s\ {}^1D_2$—$5p\ {}^3D^o_1$	
3516·95	$5s\ {}^3D_2$—$5p\ {}^3P^o_1$	
3553·10	$5s\ {}^1D_2$—$5p\ {}^1F^o_3$	
3609·56	$5s\ {}^3D_2$—$5p\ {}^3F^o_3$	
3634·70	$5s\ {}^3D_3$—$5p\ {}^3P^o_2$	

† After this paper was read before the Academy, Dempster (*Nature*, 1935, **136**, 65) reports that his mass-spectrograph has revealed six isotopes for palladium with masses 102, 104, 105, 106, 108 and 110; the four middle isotopes are about equally abundant, while the less abundant Pd 110 is more abundant than Pd 102.

‡ Kindly lent by Sir C. V. Raman, KT., F.R.S., N.L.

[6] Shenstone, *Phys. Rev.*, 1930, **36**, 669.

None of the lines above shows any isotope displacement of the even isotopes. It has therefore not been possible to determine the even isotopes of palladium or their relative abundance. A study of the known isotopes of elements in the neighbourhood of palladium shows that an odd isotope of mass number 105 should be expected to exist in palladium. Though most of the lines here examined are single, the existence of a close component ($\sim +0{\cdot}100$ cm.$^{-1}$) in a few lines renders it probable that the isotope Pd 105 with an abundance of the order of 15% has a nuclear spin $\frac{1}{2}\frac{h}{2\pi}$. The general absence of structure however indicates that the nuclear magnetic moment of Pd 105 is small. These observations in selenium and palladium support the conclusion that all nuclei with even atomic number and odd mass number have only small positive or negative magnetic moments.[7]

Gold (At. no. 79 ; At. wt. 197·2).

Frisch[8] has concluded that the resonance line of gold λ 2676 Å ($6^2S_{\frac{1}{2}}-6^2P_{\frac{1}{2}}$) is single ; Ritschl[9] finds on the other hand that the two resonance lines λ 2676 Å and 2428 Å ($6^2S_{\frac{1}{2}}-6^2P_{\frac{1}{2},\frac{3}{2}}$) are each double. The satellites are observed at $+0{\cdot}224$ cm.$^{-1}$ and at $+0{\cdot}221$ cm.$^{-1}$ in the two lines respectively. The existence of this structure has been attributed by Ritschl to a nuclear spin of $\frac{3}{2}\frac{h}{2\pi}$. Since the two above lines are resonance lines, self-absorption in the source by normal gold atoms can produce a doubling of each of the resonance lines. The present work has been undertaken with the object of deciding between these conflicting results ; it has been definitely shown that Ritschl's analysis of the resonance lines is correct. Wulff[10] has reported that his results agree with those of Ritschl ; but it has been remarked that a nuclear spin value of $\frac{5}{2}$ satisfies the interval rule better in a number of levels. In the present work the lines involving levels known to show isotope shift in the isoelectronic Hg II spectrum[11] are analysed, and it is concluded that gold consists of a single isotope of mass 197.

A hollow cathode made from a sheet of copper-gold alloy (containing about 0·5% gold) was first employed. λ 2676 Å exhibited two components of nearly equal intensity ; the possibility of this doubling arising out of self-reversal could not be ruled out. Hence the water-cooled hollow cathode previously described[1] was gold-plated on the inside ; an examination of λ 2676 Å revealed again the same two components. If the observed doublet

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7 Grace, *Phys. Rev.*, 1933, **44**, 362.
8 Frisch, *Zeits. f. Physik*, 1931, **71**, 92.
9 Ritschl, *Naturwiss.*, 1931, **19**, 690.
10 Wulff, *Phys. Rev.*, 1933, **44**, 512.
11 Venkatesachar and Sibaiya, *Proc. Ind. Acad. Sci.*, 1934, **1**, 8.

structure is not caused by any reversal, it was argued that under suitable conditions of excitation each of these components would be reversed and four lines could be observed. A thin gold sheet was therefore introduced into the hollow cathode and a discharge current of 200 mA at 1000 v. from a D. C. 1 kilowatt generator was maintained. Pl. XVI, Fig. 4 shows the doubling of each of the two real components of λ 2676 Å due to self-reversal in the source. Thus it has been established that λ 2676 Å of gold consists of two components, *viz.*, 0·000 and +0·223 cm.$^{-1}$, with an intensity ratio of about 3 : 2. The satellite separation has been computed from all the above methods, including the one giving self-reversed components.[12]

The nuclear spin of gold has to be deduced from the intensity ratio of the components; it is however difficult from visual estimates of intensities to decide between the nuclear spin values $\frac{3}{2}$ and $\frac{5}{2}$, which demand the intensity ratios to be 1·67 and 1·40 respectively. The balance of evidence is in favour of the value $\frac{3}{2}$ because the following lines involving the metastable level $5d^9\ 6s^2\ ^2D_{\frac{5}{2}}$ have the appearance of incompletely resolved flag patterns containing four components; nuclear spin values of $\frac{3}{2}$ and $\frac{5}{2}$ should yield four and six components respectively.

λ in Å.U.	Classification	Total width in cm.$^{-1}$	Interval factor of $^2D_{\frac{5}{2}}$
3029·22	$5d^9\ 6s^2\ ^2D_{\frac{5}{2}}$—$5d^9\ 6s6p\ ^2F_{\frac{7}{2}}$	0·163	0·018 cm.$^{-1}$
2748·26	$5d^9\ 6s^2\ ^2D_{\frac{5}{2}}$—$5d^9\ 6s6p\ ^4F_{\frac{7}{2}}$	0·165	

The hyperfine levels in $^2D_{\frac{5}{2}}$ are inverted.

One would expect that if gold should consist of two isotopes 197 and 199 as is suggested from its chemical atomic weight, the above lines should show the structure patterns due to the two isotopes separately. This is necessary because the $5d^9\ 6s^2\ ^2D_{\frac{5}{2}}$ level in the isoelectronic spectrum of Hg II shows large isotopic displacement. The photographs of the hyperfine structure patterns of λ 3029 Å and 2748 Å are so well exposed that even if Au 199 should exist to the extent of about 5% its presence could not have escaped notice. It must be concluded that gold consists of a single isotope of mass 197 and that its accepted chemical atomic weight is too high. Further support to this conclusion is given by the fact that an odd isotope of an element with odd atomic number has no isobare in appreciable quantity;

[12] Sibaiya, *Proc. Ind. Acad. Sci.*, 1934, **1**, 321.

Au 199, if it should exist, would be an isobare with Hg 199 (16·45%). The following table gives the percentage abundance of isobares with odd mass numbers in the heavy elements.

At. No.	Element	Percentage abundance of odd isobares				
75	Re	187 (61·8%)				
76	Os	187 (0·6%)				
79	Au		197 (100%)			
80	Hg		197 (0·01%)	203(0·006%)		
81	Tl			203 (29·4%)	205 (70·6%)	
82	Pb			203 (0·04%)	205 (0·03%)	209 (0·85%)
83	Bi					209 (100%)

Thus Au 199, if it does exist, must be present to an extent not exceeding 1% and probably it is entirely absent,* because whenever an element with odd atomic number contains two odd isotopes they will exist in comparable quantities.

The nuclear g(I) factor can be computed from Goudsmit's formula for a penetrating s-electron[13]:

$$g(\mathrm{I}) = \frac{3a}{8\mathrm{R}\propto^2} \times \frac{n_0^3}{Z_i Z_0^2} \times \frac{1838}{\mathrm{K}(j, Z_i)}.$$

For the normal $6s\,^2S_{\frac{1}{2}}$ state of gold $a = 0{\cdot}112$ cm.$^{-1}$, $n_0 = 1{\cdot}214$ and $\mathrm{K}(j, Z_i) = 2{\cdot}2$; and the g (I) value becomes 0·136 while the magnetic moment of the nucleus is 0·20. White[14] gives the nuclear magnetic moment as 1·8 after Fermi and Segre[15]; Schüler[16] however obtains the value 0·15 for the g (I) factor. My calculated value of 0·136 for the g (I) factor agrees well with the theoretical value 0·133 of Lande.[17] Using Goudsmit's formulæ for the

* More recently, Dempster (*Nature*, 1935, **136**, 65) has obtained the same result with the aid of his mass-spectrograph.

[13] Goudsmit, *Phys. Rev.*, 1933, **43**, 636.

[14] White, *Introduction to Atomic Spectra*, 1934, p. 372.

[15] Fermi and Segre, *Zeits. f. Physik*, 1933, **82**, 729.

[16] Schüler, *Zeits. f. Physik*, 1934, **88**, 323.

[17] Lande, *Phys. Rev.*, 1934, **46**, 477.

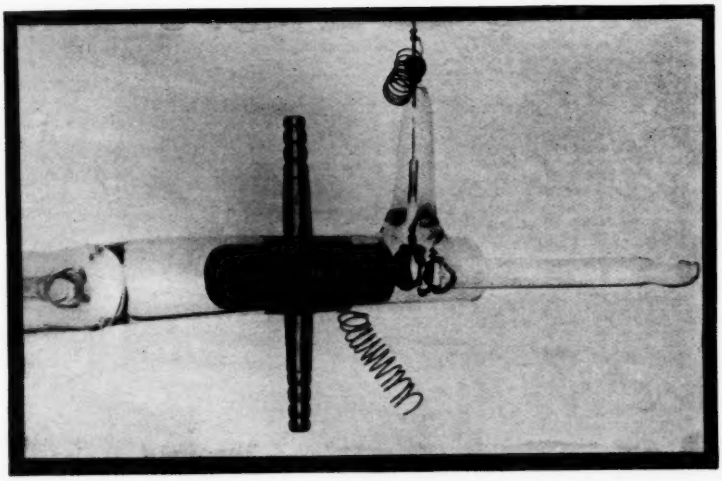

FIG. 1.

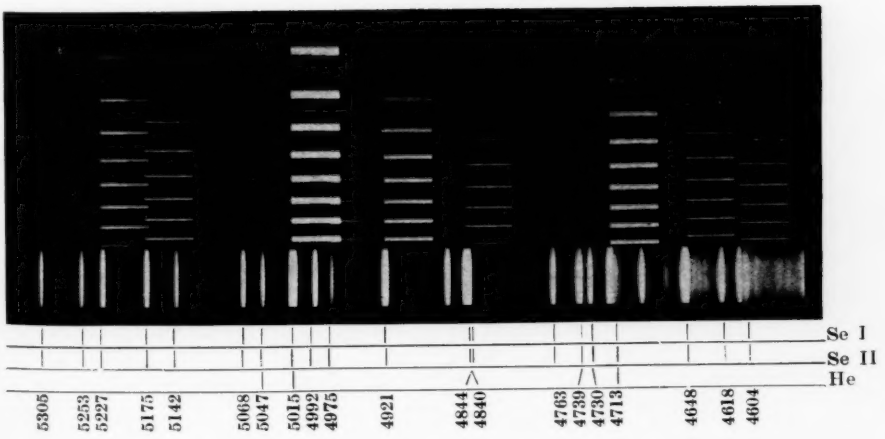
Se I
Se II
He
5305
5253
5227
5175
5142
5068
5047
5015
4992
4975
4921
4844
4840
4763
4739
4730
4713
4648
4618
4604

FIG. 2.

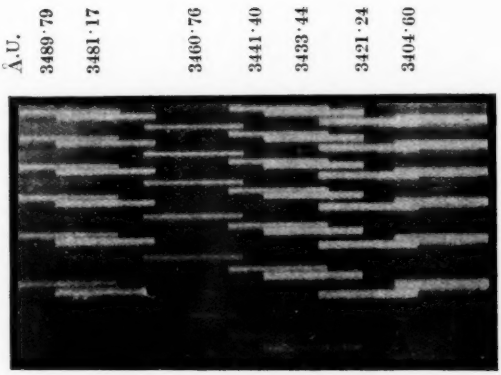

FIG. 3. Structure Pattern of Palladium Arc Lines.

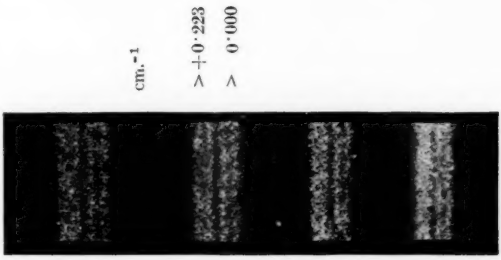

FIG. 4. Structure Pattern of Au I 2676Å ($6\,^2S_{1/2}$—$6\,^2P_{1/2}$) with each of the two components doubled by self-absorption in the source.

p-electrons it is found that the levels $5d^{10}\ 6p\ ^2P_{\frac{1}{2}, \frac{3}{2}}$ have total separations amounting to $0 \cdot 024$ cm.$^{-1}$ and $0 \cdot 008$ cm.$^{-1}$ respectively. These separations are too small to be resolved in the lines involving these levels. The larger separation ($\sim 0 \cdot 164$ cm.$^{-1}$) with an interval factor of $0 \cdot 018$ cm.$^{-1}$ in $5d^9\ 6s^2\ ^2D_{\frac{5}{2}}$ is consistent with theoretical expectations.

In conclusion I wish to thank Prof. B. Venkatesachar for his helpful guidance.

Summary.

Hyperfine structure analysis of some selenium and palladium lines shows that none of the levels examined reveal any even isotope displacement. The nuclei of Se 77 and Pd 105 have very small magnetic moments and their spin moment is probably $\frac{1}{2} \frac{h}{2\pi}$.

The doublet structure ($\Delta \nu = 0 \cdot 224$ cm.$^{-1}$) observed by Ritschl in the resonance lines of gold has been confirmed by the redoubling of each component due to self-reversal in the source ; this test proves that the originally observed doublet structure does not arise from self-reversal as the earlier results of Frisch would suggest. While in the isoelectronic spectrum of Hg II the $5d^9\ 6s^2\ ^2D_{\frac{5}{2}}$ level exhibits isotope displacement, arc lines of gold involving this level point definitely to the existence of a single isotope of mass 197 ; the accepted chemical atomic weight is therefore considered to be too high. The nuclear spin moment of gold is $\frac{3}{2} \frac{h}{2\pi}$ and the g(I) factor comes out as $0 \cdot 136$ agreeing with Lande's theoretical value.

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ON INEQUALITIES SATISFIED BY CERTAIN ARITHMETICAL FUNCTIONS (II).

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(Communicated by Dr. R. K. Asundi.)

In a previous paper[1] I proved some inequalities connected with $\aleph_\nu(x)$, $\varpi_\nu(x)$ and $\Pi_\nu(x)$. In this paper I prove some more inequalities connected with these functions.

In what follows L, N, α, β, γ denote positive absolute constants; A denotes a positive absolute constant, not necessarily the same at each occurrence. B, J and E have the same significance as in §2 and §3 of 1.

Theorem.[2]

(A. 1)' $$\aleph_{\nu+1}(x) < \frac{1}{\nu!}\frac{x}{\log x}\left(llx + \mathrm{B} + \alpha\frac{llx}{\log x}\right)^\nu \quad \text{for } x \geqslant 3 \text{; and } \nu \geqslant 1.$$

(B. 2) $$\varpi_{\nu+1}(x) < \frac{1}{\nu!}\frac{x}{\log x}\left(llx + \mathrm{B} + \mathrm{J} + \beta\frac{llx}{\log x}\right)^\nu \text{ for } x \geqslant 3\text{; and } \nu \geqslant 1.$$

(B. 1)' $$\varpi_{\nu+1}(x) < \frac{\mathrm{L}x}{\log x}\frac{(llx + \mathrm{B} + \mathrm{J})^\nu}{\nu!} \text{ for } x \geqslant 2 \text{; and } \nu \geqslant 0.$$

Let $\lambda = \cdot 57$; $\cdot 68 \leqslant \mu < 1$; $\cdot 96 \leqslant \zeta < 1$.

(C)' $$\Pi^*_{\nu+1}(x) < \frac{x}{\log x}\left\{\frac{(llx+\mathrm{B})^\nu}{\nu!} + \lambda\frac{(llx+\mathrm{B})^{\nu-1}}{(\nu-1)!} + \cdots\right\}$$
for $x \geqslant \eta$; and $\nu \geqslant 1$.

(C. 1)' $$\Pi_{\nu+1}(x) < \frac{\mathrm{N}x}{\log x}\left\{\frac{(llx+\mathrm{B})^\nu}{\nu!} + \lambda\frac{(llx+\mathrm{B})^{\nu-1}}{(\nu-1)!} + \cdots\right\}$$
for $x \geqslant 3$; and $\nu \geqslant 0$.

(C. 2) $$\Pi^*_{\nu+1}(x) < \frac{x}{\log x}\left\{\frac{(llx+\mathrm{B}+\epsilon-\mu)^\nu}{\nu!} + \mu\frac{(llx+\mathrm{B}+\epsilon-\mu)^{\nu-1}}{(\nu-1)!} + \cdots\right\}$$
for $x \geqslant \eta_1 = \eta_1(\epsilon)$; and $\nu \geqslant 1$. ϵ is any small but fixed positive number.[3]

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[1] *Indian Physico-Math. J.*, 1934, **5**, 9-16.

[2] We write *llx* for loglog x.

[3] It is easily seen that η in (C)' is independent of ν, $\eta_1 = \eta_1(\epsilon)$ in (C. 2) is independent of ν and μ, and η_2 in (C. 4) is independent of ζ and ν.

(C. 3) $\Pi_{\nu+1}(x) < \frac{x}{\log x}\left\{\frac{1}{\nu!}\left(llx+B-\mu+\gamma\frac{llx}{\log x}\right)^{\nu}+\frac{\mu}{(\nu-1)!}\right.$

$\left.\left(llx+B-\mu+\frac{\gamma llx}{\log x}\right)^{\nu-1}+\cdots\right\}$ for $x \geqslant 3$; and $\nu \geqslant 1$.

(C. 4) $\Pi_{\nu+1}(x) < \frac{x}{\log x}\left\{\frac{(llx+B-\zeta)^{\nu}}{\nu!}+\zeta\frac{(llx+B-\zeta)^{\nu-1}}{(\nu-1)!}+\cdots\right\}$

for $x \geqslant \eta_2$; and $\nu \geqslant 2$.

(C. 5) $\Pi_{\nu+1}(x) < \frac{Nx}{\log x}\left\{\frac{(llx+B-\mu)^{\nu}}{\nu!}+\mu\frac{(llx+B-\mu)^{\nu-1}}{(\nu-1)!}+\cdots\right\}$

for $x \geqslant 3$; and $\nu \geqslant 0$.

Lemma 6 below shows that it is not possible to replace $\frac{\beta llx}{\log x}$ by $\frac{\beta llx}{\log x}\frac{1}{\psi(x)}$ where $\psi(x)$ is any positive function tending to ∞ with x, in (B. 2). It is however possible to replace β by $1+\frac{A}{llx}$ and then we have

(B. 2)′ $\tilde{\omega}_{\nu+1}(x) < \frac{1}{\nu!}\frac{x}{\log x}\left(llx+B+J+\frac{llx+A}{\log x}\right)^{\nu}$

for $x \geqslant 3$; and $\nu \geqslant 1$.

A similar remark applies in the case of (A. 1)′ and (C. 3); in fact we can prove that

(A. 1)″ $\aleph_{\nu+1}(x) < \frac{x}{\nu!\log x}\left(llx+B+\frac{llx+A}{\log x}\right)^{\nu}$ for $x \geqslant 3$; and $\nu \geqslant 1$.

(C. 3)′ $\Pi_{\nu+1}(x) < \frac{x}{\log x}\left\{\frac{1}{\nu!}\left(llx+B-\mu+\frac{llx+A}{\log x}\right)^{\nu}+\frac{\mu}{(\nu-1)!}\right.$

$\left.\left(llx+B-\mu+\frac{llx+A}{\log x}\right)^{\nu-1}+\cdots\right\}$

for $x \geqslant 3$; and $\nu \geqslant 1$.

(B. 2) gives that

$\tilde{\omega}_{\nu+1}(x) \leqslant \frac{x(llx)^{\nu}}{\nu!\log x}+\frac{(B+J)\,x\,(llx)^{\nu+1}}{(\nu-1)!\log x}+0\left(\frac{x(llx)^{\nu-1}}{\log x}\right)=S$ (say) for fixed $\nu \geqslant 1$.

and anyone of the inequalities (C. 2), (C. 3) gives

$\Pi_{\nu+1}(x) \leqslant \frac{x}{\nu!}\frac{(llx)^{\nu}}{\log x}+\frac{Bx(llx)^{\nu-1}}{(\nu-1)!\log x}+0\left(\frac{x(llx)^{\nu-1}}{\log x}\right)=\Sigma$ (say) for fixed $\nu \geqslant 1$.

While it is known that[4,5]

$$\widetilde{\omega}_{\nu+1}(x) = S\,;\ \Pi_{\nu+1}(x) = \Sigma \quad \text{for fixed } \nu \geqslant 1 \qquad \ldots \qquad \ldots \qquad (a)$$

Lemma 1.

$$(1.\,1) \qquad 1 + \frac{(s+1)\,(s+6)}{10^{10}} < (1\cdot414)\left(\frac{569}{500}\right)^s \text{ for all } s \geqslant 2.$$

$$(1.\,2) \qquad \frac{s(s+1)^2}{10^{100}} < (1\cdot14)^s - (1\cdot138)^s \text{ for } s \geqslant 2.$$

Lemma 2.

Let $F_s = \sum_p \frac{1}{p^s}$

Then $F_s + \frac{s(s+1)}{2^s\cdot 10^{10}} < 2(\cdot569)^s$ for $s=2$.

$< (\cdot569)^s$ for $s \geqslant 3$.

The Lemma is easily seen to be true for $s=2$ and $s=3$. Assume it to be true for $s=n \geqslant 3$. Then,

$$\frac{(n+1)(n+2)}{2^{n+1}\cdot 10^{10}} + \frac{1}{2^{n+1}} + \frac{1}{3^{n+1}} + \text{——}.$$

$$< \frac{(n+1)\,(n+2)}{2^{n+1}\cdot 10^{10}} + \frac{1}{2^{n+1}} + \tfrac{1}{3}\left(\frac{1}{3^n} + \frac{1}{5^n} + \text{——}\right)$$

$$< \frac{(n+1)\,(n+2)}{2^{n+1}\cdot 10^{10}} + \frac{1}{2^{n+1}} + \tfrac{1}{3}\left\{(\cdot569)^n - \frac{n(n+1)}{2^n\cdot 10^{10}} - \frac{1}{2^n}\right\}$$

$$= \frac{1}{2^n\cdot 6}\left\{1 + \left(\frac{569}{500}\right)^n 2 + \frac{(n+1)(n+6)}{10^{10}}\right\}$$

$$< \frac{1}{2^n\cdot 6}\left\{(1\cdot414)\left(\frac{569}{500}\right)^n + \left(\frac{569}{500}\right)^n\cdot 2\right\} = (\cdot569)^{n+1}$$

Hence the lemma is true for $s=n+1$. $\therefore$ Q.E.D.

Lemma 3.

$$F_s + \frac{s(s+1)}{2^s\cdot 10^{10}} < (\cdot68)^s \quad \text{for } s \geqslant 2.$$

Lemma 4.

If $x \geqslant \eta_3$.

$$(1) \qquad \sum_{p^{s+1}\leqslant x} \frac{1}{p^s \log(x/p^s)} < \frac{2(\cdot569)^s}{\log x} \quad \text{for } s=2.$$

$$< \frac{(\cdot569)^s}{\log x} \quad \text{for } s \geqslant 3.$$

---

[4] S. M. Shah, "On a formulæ for $\widetilde{\omega}_\nu(x)$" (in the press).

[5] S. M. Shah, *Proc. U.P. Acad.*, 1935, **4**, 207-215. We note that $\Pi_\nu(x) \equiv \sigma_\nu(x)$ and $\widetilde{\omega}_\nu(x) \equiv \rho_\nu(x)$ (*Landau Handbuch*, 205-213).

$$(2)\quad \sum_{p^{s+1}\leqslant x} \frac{1}{p^s \log (x/p^s)} < \frac{(\cdot 68)^s}{\log x} \quad \text{for } s\geqslant 2.$$

For[6]

$$\sum_{p^{s+1}\leqslant x} \frac{1}{p^s \log (x/p^s)} < \frac{F_s}{\log x} + \frac{As(s+1)}{2^s}\frac{1}{\log^2 x} \quad \text{if } s\geqslant 2$$

$$< \frac{1}{\log x}\left\{F_s + \frac{s(s+1)}{2^s\cdot 10^{10}}\right\} \quad \text{if } x\geqslant \eta_3.$$

Hence the results follow from Lemmas (2) and (3).

Lemma 5.

$$\sum_{s\geqslant 1}\sum_{p^{s+1}\leqslant x} \frac{1}{p^s \log (x/p^s)} < \frac{llx + B + J}{\log x} + \frac{1}{\log^2 x}\left\{E_1 + \sum_{s=2}^{\infty} s \sum_p \frac{\log p}{p^s}\right\} + \frac{A}{\log^3 x}.$$

For when $s\geqslant 2$

$$\sum_{p^{s+1}\leqslant x} \frac{1}{p^s \log (x/p^s)} = \frac{1}{\log x}\left\{\sum_{p^{s+1}\leqslant x}\frac{1}{p^s} + \frac{s}{\log x}\sum_{p^{s+1}\leqslant x}\frac{\log p}{p^s} + \sum_{p^{s+1}\leqslant x}\frac{s^2\log^2 p}{p^s \log x \log (x/p^s)}\right\}$$

$$< \frac{1}{\log x}\left\{F_s + \frac{s}{\log x}\sum_p \frac{\log p}{p^s} + \sum_p \frac{s^2(s+1)\log^2 p}{p^s \log^2 x}\right\}$$

$$< \frac{1}{\log x}\left\{F_s + \frac{s}{\log x}\sum_p \frac{\log p}{p^s} + \frac{As^2(s+1)}{2^s}\frac{1}{\log^2 x}\right\}$$

$$\therefore \sum_{s\geqslant 2}\sum_{p^{s+1}\leqslant x} \frac{1}{p^s \log (x/p^s)} < \frac{J}{\log x} + \left(\sum_{s=2}^{\infty} s\sum_p \frac{\log p}{p^s}\right)\frac{1}{\log^2 x} + \frac{A}{\log^3 x}.$$

Since[7]

$$\sum_{p^2\leqslant x} \frac{1}{p \log (x/p)} < \frac{llx}{\log x} + \frac{B}{\log x} + \frac{E_1}{\log^2 x} + \frac{A}{\log^3 x} \cdots \qquad (1)$$

The lemma follows:

Lemma 6.

$$\varpi_2(x) = \frac{xllx}{\log x} + \frac{(B+J)x}{\log x} + \frac{xllx}{\log^2 x} + O\left(\frac{x}{\log^2 x}\right)$$

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[6] 1 Lemma 2.

[7] S. M. Shah, *Indian Physico-Math. J.*, 1933, **4**, 48-50; 1935, **6**, 19-25.

Proof[8]

$$\begin{aligned}
\varpi_2(x) &< \sum_{s\geqslant 1}\ \sum_{p^{s+1}\leqslant x} \varpi_1\left(\frac{x}{p^s}\right) \\
&< \sum_{p^2\leqslant x} \varpi_1\left(\frac{x}{p}\right) + \sum_{s\geqslant 2}\ \sum_{p^{s+1}\leqslant x} \frac{x}{p^s \log (x/p^s)} \\
&\quad + \mathrm{A} \sum_{s\geqslant 2}\ \sum_{p^{s+1}\leqslant x} \frac{x}{p^s \log^2 (x/p^s)} \\
&< \sum_{p^2\leqslant x} \pi\left(\frac{x}{p}\right) + \mathrm{A}x^{\frac{3}{4}} + x\left\{\frac{\mathrm{J}}{\log x} + \frac{\mathrm{A}}{\log^2 x}\right\} \\
&\quad + \mathrm{A} \sum_{s\geqslant 2} \frac{(s+1)^2}{2^s} \frac{x}{\log^2 x} \\
&< \frac{x \mathrm{ll}x}{\log x} + \frac{(\mathrm{B}+\mathrm{J})x}{\log x} + \frac{x \mathrm{ll}x}{\log^2 x} + \frac{\mathrm{A}x}{\log^2 x} \qquad \ldots \qquad \ldots \quad (2)
\end{aligned}$$

Further

$$\varpi_2(x) > \pi_2(x) + \sum_{k=2}^{\mathrm{N}} \mathrm{A}_k(x) \quad \text{where } \mathrm{N} = \left[\frac{\mathrm{ll}x}{\log 2}\right]$$

And $\mathrm{A}_k(x)$ denotes the number of integers of the form pq^k $(p \neq q)$ not exceeding x.

$$\begin{aligned}
\therefore \mathrm{A}_k(x) &= \sum_{p^k\leqslant x/2} \pi\left(\frac{x}{p^k}\right) - \pi\left(x^{\frac{1}{k+1}}\right) \\
&= \sum_{p^k\leqslant x/2} \frac{x}{p^k \log (x/p^k)} + \sum_{p^k\leqslant x/2} \frac{x}{p^k \log^2 (x/p^k)} \\
&\quad + \sum_{p^k\leqslant x/2} \mathrm{O}\left(\frac{x}{p^k \log^3 (x/p^k)}\right) - \pi\left(x^{\frac{1}{k+1}}\right) \\
&= \Sigma_1 + \Sigma_2 + \Sigma_3 - \Sigma_4
\end{aligned}$$

$$\begin{aligned}
\Sigma_1 &= \frac{x}{\log x} \sum_{p^k\leqslant x/2} \frac{1}{p^k} + \frac{x}{\log x} \sum_{p^k\leqslant x/2} \frac{k \log p}{p^k \log (x/p^k)} \\
&> \frac{x}{\log x}\left\{\sum_p \frac{1}{p^k} - \sum_{p^k > x/2} \frac{1}{p^k}\right\} + \frac{x}{\log x} \frac{k \log 2}{2^k \log (x/2^k)} \\
&> \frac{x}{\log x}\left\{\mathrm{F}_k - \frac{\mathrm{A}}{\log^3 x}\right\} + \frac{\mathrm{A}x}{\log^2 x} \frac{k}{2^k} \\
&> \frac{x}{\log x} \mathrm{F}_k - \frac{\mathrm{A}x}{\log^4 x} + \frac{\mathrm{A}x \mathrm{ll}x}{\log^3 x}
\end{aligned}$$

$$\Sigma_2 > 0\,; \quad \Sigma_3 - \Sigma_4 = \mathrm{O}\left(\frac{x}{\log^3 x}\right)$$

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[8] 1 Lemma 3.

$$\therefore A_k(x) > \frac{xF_k}{\log x} \quad \text{if } x \geqslant \eta_4.$$

$$\therefore \sum_{2}^{N} A_k(x) > \frac{x}{\log x}\left\{J - \sum_{N+1}^{\infty} F_k\right\}$$

$$\text{Now } F_k < \frac{A}{2^k} \quad \therefore \sum_{N+1}^{\infty} F_k < \frac{A}{2^N} < \frac{A}{\log x}$$

$$\therefore \sum_{2}^{N} A_k(x) > \frac{x\,J}{\log x} - \frac{A\,x}{\log^2 x} \quad \text{if } x \geqslant \eta_4.$$

$$\therefore \widetilde{\omega}_2(x) > \frac{xllx}{\log x} + \frac{(B+J)x}{\log x} + \frac{xllx}{\log^2 x} - \frac{Ax}{\log^2 x} \quad \text{if } x \geqslant \eta_4$$

which with (2) proves the lemma.

Lemma 7.

$n \geqslant 4$. For $x \geqslant \eta_5$

$$\sum_{p^n \leqslant x} \Pi_2\left(\frac{x}{p^{n-1}}\right) < (\cdot 57)^{n-1}\ \frac{x(llx + B - 1)}{\log x}$$

For

$$\sum_{p^n \leqslant x} \Pi_2\left(\frac{x}{p^{n-1}}\right) < \sum_{p^n \leqslant x} \frac{xll\left(\frac{x}{p^{n-1}}\right)}{p^{n-1}\log\left(\frac{x}{p^{n-1}}\right)} + A \sum_{p^n \leqslant x} \frac{x}{p^{n-1}\log\left(\frac{x}{p^{n-1}}\right)}$$

$$< \frac{xllx(\cdot 569)^{n-1}}{\log x} + \frac{Ax(\cdot 569)^{n-1}}{\log x} \quad \text{if } x \geqslant \eta_3.$$

Choose $\eta_5 \geqslant \text{Max}\ (\eta_3, e^e)$ so that

$$\frac{llx + A}{llx + B - 1} \leqslant \left(\frac{\cdot 57}{\cdot 569}\right) \quad \text{for } x \geqslant \eta_5.$$

Then

$$\sum_{p^n \leqslant x} \Pi_2\left(\frac{x}{p^{n-1}}\right) < \frac{x}{\log x}\,(\cdot 569)^{n-1}\,\{llx + A\}$$

$$< \frac{x}{\log x}\,(\cdot 57)^{n-1}\,(llx + B - 1) \quad \text{for } x \geqslant \eta_5.$$

Lemma 8.

$n \geqslant 4$. For $x \geqslant \eta_6$

$$\sum_{p^{n+1} \leqslant x} \Pi_1\left(\frac{x}{p^n}\right) < \frac{x(\cdot 57)^n}{\log x}$$

For

$$\sum_{p^{n+1} \leqslant x} \Pi_1\left(\frac{x}{p^n}\right) < \sum_{p^{n+1} \leqslant x} \frac{x}{p^n \log\left(\frac{x}{p^n}\right)} + Ax \sum_{p^{n+1} \leqslant x} \frac{1}{p^n \log^2\left(\frac{x}{p^n}\right)}$$

$$= x\,\Sigma_1 + A\,x\,\Sigma_2$$

$$\Sigma_2 = \frac{1}{\log^2 x} \sum_{p^{n+1} \leqslant x} \frac{1}{p^n} + \frac{1}{\log^2 x} \sum_{p^{n+1} \leqslant x} \frac{\log p^n}{p^n \log\left(\frac{x}{p^n}\right)}$$

$$+ \frac{1}{\log x} \sum_{p^{n+1} \leqslant x} \frac{\log p^n}{p^n \log^2\left(\frac{x}{p^n}\right)} = \Sigma_{21} + \Sigma_{22} + \Sigma_{23}$$

$$\Sigma_{21} < \frac{A}{2^n} \frac{1}{\log^2 x} < \frac{An\,(n+1)^2}{2^n \log^2 x}$$

$$\Sigma_{22} + \Sigma_{23} < \frac{A}{\log^2 x} \frac{n\,(n+1)^2}{2^n}$$

Choose $\eta_6 \geqslant \eta_5$ so that $\frac{2A}{\log x} < \frac{1}{10^{100}}$ for $x \geqslant \eta_6$.

Then for $x \geqslant \eta_6$

$$\sum_{p^{n+1} \leqslant x} \Pi_1\left(\frac{x}{p^n}\right) < \frac{x}{\log x}\left\{(\cdot 569)^n + \frac{2An\,(n+1)^2}{2^n \log x}\right\}$$

$$< \frac{x}{\log x}\left\{(\cdot 569)^n + \frac{n(n+1)^2}{2^n \cdot 10^{100}}\right\}$$

$$< \frac{x}{\log x}\left\{(\cdot 57)^n\right\}$$

Proof of (B. 2)

Choose η_7 so that for $x \geqslant \eta_7$

$$\widetilde{\omega}_2(x) < \frac{x}{\log x}\left\{llx + B + J + \frac{2\,llx}{\log x}\right\}$$

We prove now that for all sufficiently large values of x

$$llx + \frac{2llx}{\log x} \geqslant ll\left(\frac{x}{y}\right) + \frac{2ll\left(\frac{x}{y}\right)}{\log\left(\frac{x}{y}\right)} \quad .. \quad .. \quad .. \quad .. \quad (3)$$

where $y \equiv p^s$; $p \leqslant x^{\frac{1}{s+1}}$ and $1 \leqslant s \leqslant A \log x$.

For $p^s \leqslant x^{\frac{s}{s+1}} = x^{1-\frac{1}{s+1}}$ $\therefore \frac{x}{p^s} \geqslant x^{\frac{1}{s+1}} = e^{\frac{1}{s+1}\log x} \geqslant 1 + c > 1$.

When $1 + c \leqslant \frac{x}{y} \leqslant Allx$ then obviously (3) is satisfied if $x \geqslant \eta_8 > 3$.

When $\frac{x}{y} \geqslant Allx$ consider

$$F(y) = llx + \frac{2llx}{\log x} - ll\left(\frac{x}{y}\right)\left\{1 + \frac{2}{\log\left(\frac{x}{y}\right)}\right\}$$

$$F'(y) = \frac{1}{y \log\left(\frac{x}{y}\right)}\left\{1 + \frac{2}{\log\left(\frac{x}{y}\right)} - \frac{2ll\left(\frac{x}{y}\right)}{\log\left(\frac{x}{y}\right)}\right\} > 0 \quad \text{if } x \geqslant \eta_9.$$

$\therefore$ $F(y)$ is increasing with y. Also

$$F(2) = \frac{\log 2}{\log x} + O\left(\frac{llx}{\log^2 x}\right) > 0 \quad \text{if } x \geqslant \eta_{10}.$$

$\therefore$ (3) is satisfied for all $x \geqslant \eta_{11} = \text{Max } (\eta_8, \eta_9, \eta_{10})$.

Choose η_{12} so that for $x \geqslant \eta_{12}$

$$\sum_{s\geqslant 1} \sum_{p^{s+1}\leqslant x} \frac{1}{p^s \log\left(\frac{x}{p^s}\right)} < \frac{llx}{\log x} + \frac{(B+J)}{\log x} + \frac{2llx}{\log^2 x}$$

Let $\eta_{13} = \text{Max } (\eta_{12}, \eta_{11}, \eta_7)$ we first prove

$$\widetilde{\omega}_{\nu+1}(x) < \frac{x}{\nu!\log x}\left\{llx + B + J + \frac{2llx}{\log x}\right\}^{\nu} \text{ for } x \geqslant \eta_{13};$$

and all $\nu \geqslant 1$ .. (4)

(4) is true for $\nu = 1$. Suppose $n \geqslant 2$ and (4) to be true for $\nu = n-1$. Then

$$n\widetilde{\omega}_{n+1}(x) \leqslant \sum_{s=1}^{s=A\log x} \sum_{p^{s+1}\leqslant x} \widetilde{\omega}_n\left(\frac{x}{p^s}\right)$$

$$< \sum_{s=1}^{A\log x} \sum_{p^{s+1}\leqslant x} \frac{x}{(n-1)!\,p^s \log\left(\frac{x}{p^s}\right)} \left\{ ll\left(\frac{x}{p^s}\right) + B + J + \frac{2ll\left(\frac{x}{p^s}\right)}{\log\left(\frac{x}{p^s}\right)}\right\}^{n-1}$$

$$< \frac{x}{(n-1)!}\left\{llx + B + J + \frac{2llx}{\log x}\right\}^{n} \frac{1}{\log x}$$

which proves (4) for $\nu = n$. $\therefore$ (4) is true for $\nu \geqslant 1$.

Now $\widetilde{\omega}_{\nu+1}(x) = 0$, where $3 \leqslant x \leqslant \eta_{13}$, if ν exceeds $G = G(\eta_{13})$.

Choose $\beta = \beta(\eta_{13}) \geqslant 2$ so that

$$\widetilde{\omega}_{\nu+1}(x) < \frac{x}{\nu!\log x}\left(llx + B + J + \frac{\beta llx}{\log x}\right)^{\nu} \text{ for } 3 \leqslant x \leqslant \eta_{13}; \text{ and } 1 \leqslant \nu \leqslant G.$$

$$\therefore \widetilde{\omega}_{\nu+1}(x) < \frac{x}{\nu!\log x}\left(llx + B + J + \frac{\beta llx}{\log x}\right)^{\nu} \quad \text{for } 3 \leqslant x \leqslant \eta_{13};$$

and $\nu \geqslant 1$.

And this with (4) proves (B. 2).

Proof of (A. 1)'.

If $x \geqslant \eta_{11}$

$$ll\left(\frac{x}{p}\right) + \frac{2ll\left(\frac{x}{p}\right)}{\log\left(\frac{x}{p}\right)} \leqslant llx + \frac{2llx}{\log x} \quad \text{where } p \leqslant \sqrt{x}$$

Choose η_{14} so that

$$\Lambda_2(x) < \frac{x}{\log x}\left\{llx + B + \frac{2llx}{\log x}\right\} \quad \text{for } x \geqslant \eta_{14};$$

and η_{15} so that

$$\sum_{p^2 \leqslant x} \frac{1}{p \log \left(\frac{x}{p}\right)} < \frac{llx + B}{\log x} \quad \text{for } x \geqslant \eta_{15}.$$

Let $\eta_{16} = \text{Max}\,(\eta_{11}, \eta_{14}, \eta_{15})$ we prove then, as above, that

$$\mathcal{K}_{\nu+1}(x) < \frac{1}{\nu!} \frac{x}{\log x} \left\{ llx + B + \frac{2llx}{\log x} \right\}^{\nu} \quad \text{for } x \geqslant \eta_{16};\ \nu \geqslant 1.$$

Choosing α, as we did β, we prove (A. 1)′.

Proof of (B, 1)′.

From (B. 2)

$$\tilde{\omega}_{\nu+1}(x) < \frac{x(llx + B + J)^{\nu}}{\nu! \log x}$$

$$\times \left\{ \left(1 + \frac{\beta llx}{\log x\ (llx + B + J)}\right)^{\frac{\log x(llx+B+J)}{\beta llx}} \right\}^{\frac{\nu\beta llx}{\log x(llx+B+J)}}$$

$$< \frac{L_1 x(llx + B + J)^{\nu}}{\nu! \log x} \quad \text{for } x \geqslant 3;\ 1 \leqslant \nu \leqslant A \log x.$$

And obviously this inequality is true if $\nu > A \log x$ (absolute constant A can be so chosen that $\tilde{\omega}_{\nu+1}(x) = 0$ if $\nu > A \log x$ and $x \geqslant 2$).

Choose L_2 so that

$$\tilde{\omega}_1(x) < \frac{xL_2}{\log x} \quad \text{for } x \geqslant 2 \qquad \ldots \qquad (5)$$

Let $L = \text{Max}\,(L_1, L_2)$, then

$$\tilde{\omega}_{\nu+1}(x) < \frac{Lx}{\nu! \log x} (llx + B + J)^{\nu} \quad \text{for } x \geqslant 3;\ \text{and } \nu \geqslant 0.$$

From (5) we see that this inequality is true[9] when $2 \leqslant x \leqslant 3$ and $\nu \geqslant 0$.

$\therefore$ Q.E.D.

Proof of (C)′.

Choose η_{17} so that (C)′ is true for $x \geqslant \eta_{17}$; and $\nu = 1, 2, 3$. This is possible by (α). Let $x \geqslant \eta = \text{Max}\,(\eta_6, \eta_{17}, \eta_{15})$. Then (C)′ is true for $\nu = 1, 2, 3$. Let $n \geqslant 4$ and suppose (C)′ is true for $\nu = 1, 2, \cdots, (n-1)$. Write $llx + B \equiv \xi$. Then

$$n\Pi_{n+1}(x) < \sum_{p^2 \leqslant x} \Pi_n\left(\frac{x}{p}\right) + \sum_{p^3 \leqslant x} \Pi_{n-1}\left(\frac{x}{p^2}\right) + \cdots + \sum_{p^{n+1} \leqslant x} \Pi_1\left(\frac{x}{p^n}\right)$$

[9] We note that $ll_2 + B + J > 0$.

$$< \sum_{p^2 \leqslant x} \frac{x}{p \log\left(\frac{x}{p}\right)} \left\{ \frac{\xi^{n-1}}{(n-1)!} + \lambda \frac{\xi^{n-2}}{(n-2)!} + \cdots + \lambda^{n-1} \right\}$$

$$+ \sum_{p^3 \leqslant x} \frac{x}{p^2 \log\left(\frac{x}{p^2}\right)} \left\{ \frac{\xi^{n-2}}{(n-2)!} + \cdots + \lambda^{n-2} \right\} + \cdots + \frac{x\lambda^n}{\log x}$$

$$\therefore n\,\Pi_{n+1}(x) < \frac{x}{\log x} \left\{ \frac{\xi^n}{(n-1)!} + \cdots \right\} + \frac{2x\lambda^2}{\log x} \left\{ \frac{\xi^{n-2}}{(n-2)!} + \cdots + \lambda^{n-2} \right\}$$

$$+ \frac{x\lambda^3}{\log x} \left\{ \frac{\xi^{n-3}}{(n-3)!} + \cdots \right\} + \cdots + \frac{x\lambda^n}{\log x}$$

$$\therefore \Pi_{n+1}(x) < \frac{x}{\log x} \left\{ \frac{\xi^n}{n!} + \lambda \frac{\xi^{n-1}}{(n-1)!} + \cdots + \lambda^n \right\}$$ which proves (C)'

for $\nu = n$. ∴ Q.E.D.

(C. 1)' follows easily from (C)'.

Proof of (C. 2).

Given ϵ choose $\eta_{18} = \eta_{18}(\epsilon)$ so that (C. 2) is true for $x \geqslant \eta_{18}$; and $\nu = 1, 2, 3$.

Let $x \geqslant \eta_1 = \text{Max}(\eta_{18}, \eta_6, \eta_{15})$. Then (C. 2) is true for $\nu = 1, 2, 3$. Let $n \geqslant 4$ and suppose (C. 2) to be true for $\nu = 1, 2, \cdots, (n-1)$. Write $llx + \text{B} + \epsilon - \mu = \xi$.

$$n\,\Pi_{n+1}(x) < \sum_{p^2 \leqslant x} \frac{x}{p \log\left(\frac{x}{p}\right)} \left\{ \frac{\xi^{n-1}}{(n-1)!} + \mu \frac{\xi^{n-2}}{(n-2)!} + \cdots \right\}$$

$$+ \sum_{p^3 \leqslant x} \frac{x}{p^2 \log\left(\frac{x}{p^2}\right)} \left\{ \frac{\xi^{n-2}}{(n-2)!} + \cdots \right\} + \cdots + \frac{x\mu^n}{\log x}$$

$$< \frac{x}{\log x} \left\{ \xi + \mu - \epsilon \right\} \left\{ \frac{\xi^{n-1}}{(n-1)!} + \cdots \right\} + \frac{x}{\log x} \mu^2 \left\{ \frac{\xi^{n-2}}{(n-2)!} + \cdots \right\} + \cdots$$

$$= \frac{x}{\log x} \left\{ \frac{\xi^n}{(n-1)!} + \xi^{n-1} \frac{(n\mu - \epsilon)}{(n-1)!} + \cdots + \xi^{n-k} \frac{(n\mu - \epsilon)\mu^{k-1}}{(n-k)!} + \cdots \right.$$

$$\left. + \cdots + \frac{\xi(n\mu - \epsilon)\mu^{n-2}}{1!} \right\} + \frac{x}{\log x} \left\{ (\mu - \epsilon)\,\mu^{n-1} + (n-1)\mu^n \right\}$$

$$\therefore \Pi_{n+1}(x) < \frac{x}{\log x} \left\{ \frac{\xi^n}{n!} + \mu \frac{\xi^{n-1}}{(n-1)!} + \cdots \mu^n \right\}$$

which proves (C. 2) for $\nu = n$ ∴ Q.E.D.

The proof of (C. 3) is similar to that of (C. 2). See also the proof of (B. 2).

(C. 4).

Since[10] $\Pi_n(x) - \nearrow_n(x) \sim \frac{xF_2}{\log x} \cdot \frac{(llx)^{n-3}}{(n-3)!}$ for fixed $n \geqslant 3$ .. (β)

$\therefore$ Choose η_{19} so that (C. 4) is true for $x \geqslant \eta_{19}$ and $\nu = 2, 3$. This is possible by (β) and (A. 1)'.

Let $x \geqslant \eta_2 = \text{Max}\ (\eta_{19}, \eta_{15}, \eta_6)$. Then (C. 4) is true for $\nu = 2, 3$. The proof is now similar to that of (C. 2).

Proof of (C. 5).

Choose N_1 so that

$$\Pi_1(x) < \frac{N_1 x}{\log x} \quad \text{for } x \geqslant 3$$

And $N_2 \geqslant N_1$ so that $\Pi_2(x) < \frac{N_2 x}{\log x}\{llx + B\}$ for $x \geqslant 3$.

We first prove that

$$\Pi_{\nu+1}(x) < \frac{N_2 x}{\log x}\left\{\frac{(llx + B - \mu)^\nu}{\nu!} + \mu\frac{(llx + B - \mu)^{\nu-1}}{(\nu-1)!} + \cdots\right\}$$

for $x \geqslant \eta_{20} = \text{Max}\ (\eta_{15}, \eta_3, e^e)$; and $\nu \geqslant 0$ .. .. .. (6)

(6) is true for $\nu = 0$ and $\nu = 1$. Let $n \geqslant 2$ and suppose (6) to be true for $\nu = 1, 2, \cdots, (n-1)$. Write $llx + B - \mu = \xi$. Then,

$$n\Pi_{n+1}(x) < N_2\left[\sum_{p^2 \leqslant x} \frac{x}{p \log\left(\frac{x}{p}\right)}\left\{\frac{\xi^{n-1}}{(n-1)!} + \mu\frac{\xi^{n-2}}{(n-2)!} + \cdots\right\}\right.$$

$$\left. + \sum_{p^3 \leqslant x} \frac{x}{p^2 \log\left(\frac{x}{p^2}\right)}\left\{\frac{\xi^{n-2}}{(n-2)!} + \cdots\right\} + \cdots + \sum_{p^{n+1} \leqslant x} \frac{x}{p^n \log\left(\frac{x}{p^n}\right)}\right]$$

$$< \frac{N_2 x}{\log x}\left[(\xi + \mu)\left(\frac{\xi^{n-1}}{(n-1)!} + \cdots\right) + \mu^2\left(\frac{\xi^{n-2}}{(n-2)!} + \cdots\right) + \cdots + \mu^n\right]$$

$$\therefore\ \Pi_{n+1}(x) < \frac{N_2 x}{\log x}\left\{\frac{\xi^n}{n!} + \mu\frac{\xi^{n-1}}{(n-1)!} + \cdots \mu^n\right\}$$

which proves it for $\nu = n$.

Hence (6) is true for $x \geqslant \eta_{20}$; and $\nu \geqslant 0$.

Now consider when $3 \leqslant x \leqslant \eta_{20}$. If $e^e \leqslant x \leqslant \eta_{20}$ each term in the bracket of (6) is positive. If $3 \leqslant x \leqslant e^e$ the bracket

$$= \left\{\mu^{\nu-1}\left(\mu + \frac{llx + B - \mu}{1}\right) + \frac{\mu^{\nu-3}}{2!}(llx + B - \mu)^2\left(\mu + \frac{llx + B - \mu}{3}\right) + \cdots\right.$$

$$\left. + \cdots + \frac{(llx + B - \mu)^{\nu-1}}{(\nu-1)!}\left(\mu + \frac{llx + B - \mu}{\nu}\right)\right\} \quad \text{if } \nu \text{ is odd.}$$

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[10] S. M. Shah, "On the Difference $[\sigma_n(x) - \nearrow_n(x)]$" (in the press).

$$= \left\{\mu^{\nu-1}\left(\mu + \frac{llx+B-\mu}{1}\right) + \cdots + \cdots + \frac{(llx+B-\mu)^{\nu}}{\nu!}\right\} \quad \text{if } \nu \text{ is even.}$$

Hence R.H.S. of (6) is positive when $3 \leqslant x \leqslant \eta_{20}$.

Further $\Pi_{\nu+1}(x) = 0$, when $3 \leqslant x \leqslant \eta_{20}$, if ν exceeds G (η_{20}).

Choose $N_3 = N_3(\eta_{20})$ such that

$$\Pi_{\nu+1}(x) < \frac{N_3 x}{\log x}\left\{\frac{(llx+B-\mu)^{\nu}}{\nu!} + \mu\frac{(llx+B-\mu)^{\nu-1}}{(\nu-1)!} + \cdots\right\}$$

for $3 \leqslant x \leqslant \eta_{20}$; and $0 \leqslant \nu \leqslant G$ .. .. (7)

and (7) is certainly true for $3 \leqslant x \leqslant \eta_{20}$; and $\nu > G$. Let $N = \text{Max}\,(N_2, N_3)$. Then from (6)

$$\Pi_{\nu+1}(x) < \frac{Nx}{\log x}\left\{\frac{(llx+B-\mu)^{\nu}}{\nu!} + \mu\frac{(llx+B-\mu)^{\nu-1}}{(\nu-1)!} + \cdots\right\}$$

for $x \geqslant 3$; and $\nu \geqslant 0$. $\therefore$ Q.E.D.

AN AFFINE CALCULUS OF VARIATIONS.

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I use the word *affine* here in the sense of *non-metric*, and not with reference to the transformation group of a parameter. More specifically, we shall deal with the differential geometry of a system of n equations of order $\sigma+1$:

(I) $x^{(\sigma+1)} + \alpha^i\,(x,\ x^{(1)},\ x^{(2)},\ \cdots,\ x^{\sigma},\ t) = 0 \quad (i = 1,\ 2,\ \cdots,\ n.)$

Besides the tensor summation convention, we shall use the notation:

$$u^{(0)i} = u^i \qquad u^{\nu i} = u^{(\nu)i} = \frac{du^{(\nu-1)i}}{dt} \qquad f_{,i} = f_{(0)i} = \frac{\partial f}{\partial x^i} \qquad f_{\nu i} = f_{(\nu)i} = \frac{\partial f}{\partial x^{\nu i}}$$

Greek indices, when summed, will range over the values 0, 1, 2, $\cdots$, σ.

We may assume various kinds of parallelisms or differential operators for this geometry. But it will be seen[1] that the simplest differential operator which carries a tensor into another of the same rank and is distributive in addition, is necessarily of the type

$$(1) \qquad \mathcal{D}u^i = \frac{du^i}{dt} + \gamma^i{}_r u^r \qquad \frac{d}{dt} = -\alpha^r\ \frac{\partial}{\partial x^{\sigma r}} + \sum_{\nu=0}^{\sigma-1} x^{(\nu+1)r}\ \frac{\partial}{\partial x^{\nu r}},$$

where the coefficients $\gamma^i{}_j$ have the proper law of transformation when coordinates undergo a non-singular change independent of the absolute parameter t. The difference of any two sets of coefficients $\gamma^i{}_j - \gamma'^i{}_j$ would be a tensor of the rank indicated as an invariant of the connection. But to determine an *intrinsic* connection and the set of differential invariants arising therefrom, we shall have to refer to the equations of variation of (I), *i.e.*,

(II) $u^{(\sigma+1)i} + u^{\nu r}\alpha^i{}_{\nu r} = 0$

(I) and (II) are assumed, of course, to be tensor invariant in form, with u^i a vector variation which carries *paths* [solutions of (I)] into other paths, when multiplied by an infinitesimal factor as usual. To bring out the tensor invariance of (II), they may be written in the form

$$(2) \qquad \mathcal{D}^{(\sigma+1)}u^i + \mathcal{D}^{\nu}u^r\ \underset{(\nu)}{\mathrm{P}}{}^i{}_r = 0 \qquad \mathcal{D}^{\nu} = \mathcal{D}(\mathcal{D}^{\nu-1}), \text{ etc.}$$

The coefficient of $\mathcal{D}^{\sigma}u^r$ is $\underset{(\sigma)}{\mathrm{P}}{}^i{}_r = \alpha^i{}_{\sigma r} - (\sigma+1)\gamma^i{}_r$. If this is taken to be zero, the intrinsic connection is at once determined as $\gamma^i{}_j = \frac{1}{\sigma+1}\,\alpha^i{}_j$. The

[1] D. D. Kosambi, "Parallelism and Path-Spaces," *Math. Zeit.*, 1933, pp. 608-618.

remaining coefficients $\underset{(0)}{P^i_j}$, $\underset{(1)}{P^i_j}$, $\cdots$, $\underset{(\sigma-1)}{P^i_j}$ calculated with this determination of the connection, are intrinsic differential invariants of the space, occupying the position of primary curvature tensors. The full set of differential invariants may be obtained by alternating the fundamental differential operations

$$\frac{\partial}{\partial x^\sigma} \qquad \mathcal{D} \qquad \frac{\partial}{\partial t}$$

It is the first two that are most productive; we obtain a secondary set of differential operators corresponding to the ordinary covariant derivative:

$$\begin{aligned}
&\underset{(1)}{\nabla_j} u^k = (\mathcal{D}u^k)_{\sigma_j} - \mathcal{D}u^k{}_{\sigma_j} \\
(3) \qquad &\underset{(2)}{\nabla_j} u^k = \underset{(1)}{\nabla_j} \mathcal{D}u^k - \mathcal{D} \underset{(1)}{\nabla_j} u^k \\
&\cdots\cdots\cdots\cdots \\
&\underset{(\sigma)}{\nabla_j} u^k = \underset{(\sigma-1)}{\nabla_j} \mathcal{D}u^k - \mathcal{D} \underset{(\sigma-1)}{\nabla} u^k
\end{aligned}$$

In the actual computation of each of these, it must be noted that certain tensorial terms may occur, due to the fact that $a^i{}_{\sigma j \sigma k}$ is a tensor of the space when the order $\sigma+1$ is greater than two. Such terms are left out altogether without affecting the tensorial nature of the operation. The operators $\underset{(\nu)}{\nabla_j}$ as well as $\mathcal{D}$ are extensible to tensors of any rank, as in the usual covariant differentiation. It should be noted that whereas only $\partial/\partial x^{(\sigma)}$ is tensorial, any $\partial/\partial x^\nu$ will give a tensor with an additional covariant index when applied to a tensor containing no higher derivative of x^i than $x^{\nu i}$. But the general processes are as given above.

Further alternations of the primary and secondary differential operators will give relations involving these operators with coefficients which give the differential invariants of the space, of which a full set may thus be obtained. The $\underset{(\nu)}{P^i_j}$ and $a^i{}_{\sigma j \sigma k}$ with $x^{(1)i}$ itself constitute the primary set, when $\sigma > 1$.

The calculus of variations has always been a guide in the construction of such generalized differential geometries. It corresponds to the metric case. A necessary condition for the existence of a metric is that the equations (II) be self-adjoint. It is, presumably, a sufficient condition also, though the general theorem is not easy to prove. For $\sigma = 1$, it has been demonstrated, and, for that matter, the complete differential geometry of the space has been worked out on the lines sketched above.[2] I treat here

[2] D. D. Kosambi, "Systems of Differential Equations of the Second Order," *Quarterly Journal of Math.*, Oxford Series, 1935, pp. 1-12.

the case $\sigma = 0$, as it is so simple as to give only a few of the features of a complete differential geometry, and for that reason, will not be considered elsewhere.

The paths being given by

$$\frac{dx^i}{dt} + a^i(x, t) = 0 \qquad i = 1, 2, \cdots, n$$

the vector a^i itself is the essential differential invariant of the space. If now a tensor f_{ij} be sought which associates covariant and contravariant indices according to the usual law, the equations of variation of

$$f_{ir}\{\dot{x}^r + a^r\} = 0$$

become self-adjoint if and only if

$$(4) \quad f_{ij} + f_{ji} = 0$$

$$(5) \quad f_{ij,k} + f_{jk,i} + f_{ki,j} = 0$$

$$(6) \quad -a^k f_{ij,k} + \frac{\partial}{\partial t} f_{ij} - f_{ik}\, a^k{}_{,j} - f_{kj}\, a^k{}_{,i} = 0$$

Of these, (4) and (5) show that f_{ij} must be the curl of a vector. Moreover, n, the number of dimensions of the space, must be even, if the skew-symmetric determinant $|f_{ij}|$ is not to vanish identically. Writing the fundamental tensor as $f_{ij} = \phi_{i,j} - \phi_{j,i}$ where ϕ_i is a function of x, t, we see from (6) that $(f_{ir}a^r)_{,j} - (f_{jr}a^r)_{,i} = \frac{\partial}{\partial t} f_{ij}$ which indicates that $f_{ir}a^r - \frac{\partial}{\partial t}\phi_i$ is a partial derivative, $-\psi_{,i}$. The integrand of the variational problem is obtained at once, and the paths are the extremals of $\delta\int(\phi_r \dot{x}^r + \psi)dt = 0$.

A SIMPLE TEST OF VALUE OF A PARTICULAR PERIOD IN FORECASTING.

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Received August 2, 1935.

In an interesting paper "Sunspots and Weather"[1] C. G. Abbot has come to the conclusion that "weather repeats itself in all parts of the world with 23-year intervals". As regards the use of this cycle for weather predictions he says, "At many stations this cycle in weather enables us to forecast general conditions of temperature and precipitation for many years in advance. Accurate seasonal predictions would require a more complete knowledge of the causes of shifts of phase in weather periodicities than is yet available." This raises the following interesting question :—"If a periodicity is known to exist in some known data, what should the other conditions, apart from changes in phase, be in order that the periodicity may be of use in forecasting the data ?" To solve this question we may proceed as follows :

We will assume for the present that there are no shifts of phase as contemplated by Abbot. Let there be an n-year periodicity whose effect in the data is represented by $a_1, a_2, \ldots\ldots, a_{n-1}$ and a_n. The actual values will then be $a_1+d_1, a_2+d_2, \ldots\ldots, a_n+d_n, a_1+d_{n+1}, a_2+d_{n+2}, \ldots\ldots$, where $d_1, d_2, \ldots$ are random variations which are independent of the a's. Without loss of generality we can assume that μ_d, the mean of the d-population, is zero. The $(f+kn)$th value is easily seen to be $a_f+d_{(f+kn)}$, where f and k are positive integers and $0<f<n+1$. The deviations, d, arising from unknown causes cannot be forecasted. This shows that accurate predictions are not possible. If, however, we are content with a forecast having an 80% chance of success, we can predict that the $(f+kn)$th value lies between $a_f \pm c$, where c is such a value that the chance of a random deviation d not exceeding c numerically is 80%. c can be determined when the frequency curve of the d-population is known.

In order that our forecast may be *useful*, it is essential that $\sigma_a < \sigma_d$* and the interval, $2c$, between our forecasted limits should be a small fraction of a_f. Since the value of a_f is different for different years, we may take its

* Otherwise the random variations become more predominant than the periodical variations. σ_a and σ_d are the population standard deviations of the a's and the d's respectively.

least value, a_l, and demand that $2c$ must be less than say 10% of a_l; *i.e.*,

$$2c < \frac{1}{10} a_l \quad .. \quad .. \quad .. \quad .. \quad \text{I.}$$

We may not be far wrong if we suppose that the d's belong to a normal population. In this case $c = 1 \cdot 28\sigma_d$ where σ_d is the standard deviation of the d-population as mentioned above. Equation I now becomes

$$\frac{\sigma_d}{a_l} < 0 \cdot 039 \quad .. \quad .. \quad .. \quad .. \quad \text{II.}$$

In order to give a forecast with an 80% chance of success, we should know σ_d and $a_1, a_2, \ldots\ldots, a_{n-1}$ and a_n. In practice, however, we do not know these quantities, but only the observed values, namely, $a_1+d_1, a_2+d_2, \ldots\ldots$ To determine the values a_1, a_2, etc., we may proceed as follows :

Let the observed values be denoted by $e_1, e_2, \ldots\ldots$ We arrange these values in the following manner :

	e_1	e_2	.. .. ..	e_n
	e_{n+1}	e_{n+2}	.. .. ..	e_{2n}
	..	..	.. .. ..	..
	..	..	.. .. ..	..
	..	..	.. .. ..	..
	e_{gn-n+1}	e_{gn-n+2}	.. .. ..	e_{gn}
Sum ..	s_1	s_2	.. .. ..	s_n
Mean $\left(=\frac{s}{g}\right)$	m_1	m_2	.. .. ..	m_n

The values m_1, m_2, etc., are our estimates of $a_1, a_2, \ldots\ldots$, respectively. It is clear that as g tends to infinity, the values $m_1, m_2, \ldots\ldots$, tend respectively to $a_1, a_2, \ldots\ldots$ It is easy to see that the standard error of the m's is very approximately equal to $\sigma_d/\sqrt{g}$ when n is not small. Hence the highest random error (on the 5% level, that may be expected in the m's is $0 \cdot 674 \times p \times \frac{\sigma_d}{\sqrt{g}}$, where p is the value of A_1 corresponding to $M = n$ taken from Table I of (2). This error should be comparatively small. Let us

say that it should not be greater than 1/15 of the true value of the least of the a's. That is

$$0{\cdot}674 \times p \times \sigma_d / \sqrt{g} \leqslant \frac{1}{15}\, a_l$$

or

$$\frac{\sigma_d}{a_l} \leqslant \frac{\sqrt{g}}{10{\cdot}1p} \quad .. \quad .. \quad .. \quad .. \quad \text{III.}$$

Comparing this with equation II we see that

$$\frac{\sqrt{g}}{10{\cdot}1p} \geqslant 0{\cdot}039$$

or

$$g \geqslant 0{\cdot}155\, p^2 \quad .. \quad .. \quad .. \quad .. \quad \text{IV.}$$

For example, when $n=23$, $p=4{\cdot}5$ from Table I of (2). $\therefore g \geqslant 3{\cdot}14$, *i.e.*, the number of rows must be greater than 3. In this particular case we may be satisfied with $g=3$.

It is hardly necessary to repeat that the greater g is, the more accurate do the values of m become.

We assumed above that an n-year periodicity exists in the data. The real difficulty is to find out whether our assumption is correct. We can, however, test its accuracy in the following manner:

We assume the existence of the n-year period and calculate the means $m_1, m_2, \ldots\ldots$, as explained above. In calculating these means we use as many of the data as are necessary to give us at least g rows, the value of g being that given by relation IV above, and such that not less than 17 values lie over. The reason for at least 17 values remaining over is given later on. Our periodic values are, as has already been said, $m_1, m_2, \ldots\ldots$ We now test these values against the actual values *which were not used in calculating the means* $m_1, \ldots\ldots$ In doing so we will be using a form of the Performance Test suggested by C. W. B. Normand.[3,4] The method of testing is as follows. Let the successive actual values not used in calculating m_1, etc., be denoted by $A_1, A_2, \ldots\ldots, A_s$. We correlate these with our forecasted values $m_1, m_2, \ldots\ldots$ *The* n*-year periodicity can be considered to be real only when the correlation coefficient* (*which may be called the test correlation coefficient or briefly the test* r) *is not only significant, but positive as well.*[4]

Having proved in this or any other equally trustworthy manner that the periodicity is real, we can easily test whether it will be of use for forecasting purposes in the following way:

We compute $\delta_1 = e_1 - m_1$, $\delta_2 = e_2 - m_2$, $\ldots\ldots$, $\delta_n = e_n - m_n$, $\delta_{n+1} = e_{n+1} - m_1$ $\ldots\ldots$ These δ's are our approximations to the corresponding d's. If corresponding to equation II we find that $s_\delta / m_l < 0{\cdot}039$ where s_δ is the

standard deviation of the δ's and m_l, the least value of the m's, we can take it that the periodicity will be useful for forecasting purposes.

The reason for allowing at least 17 of the original values to remain over may be seen from the following. When a significant periodicity does exist, we may assume that the least value of ρ_{mA}, *i.e.*, the population-correlation between the m's and the A's, is about ·8.† The value of Fisher's z corresponding to this value of ρ is 1·1, see[5]. Since our sample contains s values, the standard error of the z for our sample is $1/\sqrt{s-3}$. Hence the least "probable value" of z on the 5% level of significance that we may expect in our sample is $1 \cdot 1 - 2/\sqrt{s-3}$.

If the m's and the A's are uncorrelated, the highest "probable value" of z, again on the 5% level, is $2/\sqrt{s-3}$. Hence in order that our value of z may be considered significant $1 \cdot 1 - 2/\sqrt{s-3}$ should be greater than $2/\sqrt{s-3}$, *i.e.*, s should be greater than 16·3.

Thus the least value of s is 17.

The method detailed above was first tested on artificial sets of data obtained in the following manner. From one of the *Sankhya* tables of random sample deviations from the mean of a normal population[6] a set of 23 values was taken.‡ To each of these values was added 5, the resulting values thus constituting a random set of 23 from a normal population of $\mu=5$ and $\sigma=1$. One set of such values were :

4·46, 4·79, 4·40, 3·41, 4·40, 5·22, 6·45, 4·16,
6·71, 5·93, 5·17, 3·73, 5·48, 4·17, 5·14, 4·88,
4·34, 5·50, 5·93, 5·81, 6·54, 4·60, 6·24 .. .. V.

These values were taken as our a's, the periodic values. Since the least value in this set is 3·41, we see from equation II that σ_d should be less than 0·133. We therefore took $\sigma_d=0 \cdot 12$ and multiplied by this quantity every value in another set of 112 figures taken from [6]. These were our d's. To these were added the periodic values a's given in V and we thus obtained a set of 112 values in which random variations were superposed upon a 23-interval period, this set satisfying the conditions necessary for a "useful" forecast.

Using 92 values of these so as to give us 4 rows, the values m_1, m_2, ..., m_{23} were determined. These were correlated with the remaining 20 values of the original data.

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† The value of the correlation coefficient depends in a complicated way upon σ_a, σ_d and g. This relation is being investigated separately in another connection.

‡ These values were approximated to two places of decimals to lighten calculation.

The test correlation coefficient was $+0\cdot99$.

This very high value of the test r is no doubt due to the fact that σ_a, in the above set of values, is nearly 9 times σ_d.

In another set of data in which $\sigma_a = \sigma_d$, as an extreme case, the test r was $+0\cdot64 \pm 0\cdot09$.§ In both these cases the test r's show that the periodicity does exist which was further tested and found to be useful for forecasting purposes.

The method was then applied to three other sets of data taken from [6] in which there was no periodicity at all, the period tested being the 23-interval period. The test r's were $+0\cdot21 \pm 0\cdot15$, $-0\cdot06 \pm 0\cdot24$ and $-0\cdot24 \pm 0\cdot14$, showing, as it should, that there is no significant 23-interval period in the data, and hence the periodicity is of no use for forecasting purposes.

This test, having thus been proved to be reliable, was applied to the annual rainfall at Madras which is available from 1813. The period tested was again the 23-year period which is considered to be the most important by Abbot as regards weather phenomena. In the case of Madras we could make g as high as 4. The correlation coefficient obtained was, however, only $0\cdot113$ and *negative* in sign, showing that the 23-year period is of no use in forecasting the annual rainfall at Madras.

Abbot in his paper[1] finds that the 23-year period is well marked in the annual rainfall at Nagpur. This rainfall is available from 1855. On applying this test to this set of data, the correlation coefficient was found to be *negative* and of magnitude $0\cdot14$, showing again that the 23-year period is not of use in forecasting the annual rainfall at Nagpur.

It has already been mentioned that in this test the change of phase has not been taken into account. The following are the reasons: In the first place, it is difficult to say when exactly the phase changes suddenly and by what amount. Secondly, even if these two could be determined in the data already available, either by inspection or by any other method, it does not seem possible at present to say when in future the phase will change again and by how much. If by some means we are able to do so in future, then our test can be easily modified to take into account the various sudden changes of phase. All that we need do is to see that the data in any column are all of the same phase, in which case we will obtain more accurate values of the means which will be of use in forecasting. It is to be hoped that the investigations of Abbot[1] will throw light on these changes of phase.

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§ 0.09 is the "probable error".

In conclusion I wish to thank Dr. C. W. B. Normand, Director-General of Observatories, Poona, for the kind interest he has taken in this piece of work.

Summary.

A simple method of testing whether a particular period is of use in forecasting is explained. The method was first tested on artificial sets of data in two of which random variations were superposed upon a periodic variation, and in the remaining three there were no periodicities at all. In the former case the periodicity tested was found to be significant, while in the latter the periodicity was not significant. When the same method was applied to see whether the 23-year period, suggested by C. G. Abbot, would be of use in forecasting annual rainfall at Madras and Nagpur, it was found that the period is not of use.

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ROTATIONAL RAMAN SCATTERING IN BENZENE.

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A series of experimental investigations by Weiler (1931), Ranganadham (1932), Bhagavantam (1933), Rao (1934) and others have shown that the rotational Raman bands in liquids start with a maximum intensity at the centre of the Rayleigh line contrary to the case of gases. In the latter the bands start with zero intensity at the centre of the Rayleigh line and exhibit a maximum intensity only at some distance from it. In these investigations, although instruments of very different dispersions and optical qualities have been used on different occasions, the results were always reproduced in a most satisfactory manner. Recently, however, Sirkar and Maiti (1935) claimed to have obtained different results with liquid benzene by using improved experimental technique. These authors used a Fuess glass spectrograph and after employing a correction for the broadening of the Rayleigh line, obtained an intensity distribution similar to that obtained in gases. It is apparent from the microphotometric curves reproduced by these authors that the instrument which they have employed is not of a very high dispersion and the exposure conditions are such that the procedure adopted by them for eliminating the line broadening is hardly likely to yield any reliable results.

About the same time as that of the publication of these results, the author had obtained some very good photographs of the Raman spectrum of benzene in another connection using a high dispersion instrument (Hilger E. I. with glass parts) placed very kindly at his disposal by Sir C. V. Raman, at the Indian Institute of Science, Bangalore. The dispersion of this instrument (about 5 A.U. per mm. in the blue) is so great and the Rayleigh lines so sharp that if there existed a maximum intensity in the rotation wing at a distance of 18 wave-numbers it should at once have been apparent in the photographs themselves but no such thing was seen. Intensity marks have been recorded in the usual way on the same plate by the method of varying slit widths and a quantitative investigation made of the distribution of intensity within the wing. The results agree so perfectly with those obtained earlier using instruments of much lower dispersion and optical quality that ordinarily there would

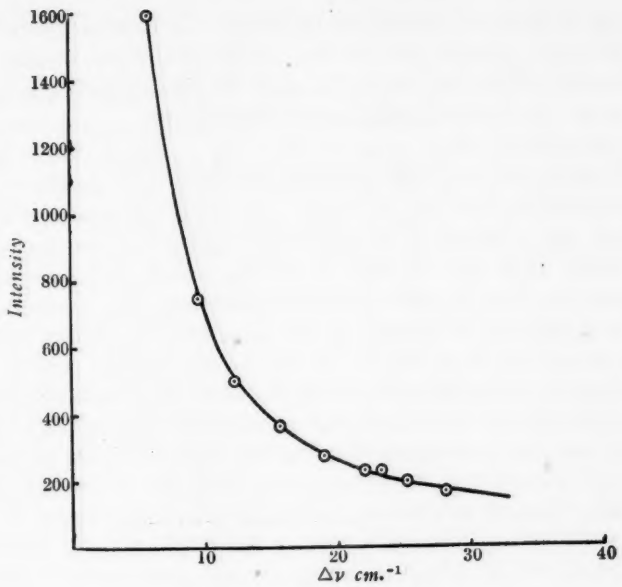
1600
1400
1200
1000
800
600
400
200
Intensity
10
20
30
40
Δν cm.⁻¹

FIG. 1.

FIG. 2.

have been no necessity of publishing the same. In view of the recent work of Sirkar and Maiti, a publication of these results is however sought here.

The continuous curve in Fig. 1 is taken from Rao (1934) and the circles with dots inset represent the values obtained in the present investigation. Fig. 2 is a microphotometric record of the wing on either side of the λ 4358 line and the arrow indicates the position at which one should expect the maximum intensity in the wing to occur. The large dispersion of the instrument renders this position to be distinctly separated from the centre and direct exposures show that the line never broadens to such an extent. The perfect agreement between the results obtained with this instrument where questions of background correction do not arise at all in regions further than about 8 wave numbers from the centre and the older results cannot be fortuitous. If we are to accept Sirkar and Maiti's results, the absence of a maximum or a discontinuity in the microphotometric record in the position of the arrow can only be explained by saying that the Rayleigh line itself has broadened due merely to overexposure to the extent of about 18 cm.$^{-1}$ or more on either side, *i.e.*, has a breadth of 1·5 mm. excluding the wing. Such is certainly not the case for this instrument. Figs. 1 and 2 which have been obtained under conditions which eliminate altogether the necessity of correcting for a background are to be regarded as much more reliable than the results obtained with a Fuess spectrograph after applying a correction for the broadening of the Rayleigh line which itself forms a good part of the recorded wing.

In conclusion the author desires to express his grateful thanks to Sir C. V. Raman for his kind interest in the work.

Summary.

A study of the intensity distribution in the rotation wing accompanying the Rayleigh lines in liquid benzene is made using a high dispersion spectrograph. The results are in perfect agreement with those obtained on earlier occasions using instruments of lower dispersion.

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X-RAY ANALYSIS OF THE STRUCTURE OF IRIDESCENT SHELLS.

Part II.—The *Haliotidæ*.

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1. *Introduction.*

In an earlier paper[1] the previous X-ray investigations of mother-of-pearl were reviewed and the results of an X-ray study of the nature of the nacreous layer of some aragonitic iridescent shells put forward and discussed. The shells studied were *Trochus* and *Turbo* species among the Gastropods, *Margaratifera vulgaris* and *Mytilus viridis* among the Bi-valves and *Nautilus pompilius* among the Cephalopods. With the X-rays incident parallel to the surface, all of them gave spot patterns. But with the X-rays incident normally, the Bi-valves gave spot patterns with only one axis of symmetry and the Gastropods *Turbo* sp. and *Trochus* sp. gave complete ring systems like those of a powder pattern. *Nautilus pompilius*, on the other hand, gave a spot pattern which was highly symmetrical about both the horizontal and the vertical axes. From a study of these patterns and others obtained with the X-rays incident parallel to the surface at various inclinations to the lines of growth it was suggested that the *c* axis of the aragonite crystallites in the nacreous layer is normal to the shell surface in all cases. Further it was suggested that the other two axes are randomly oriented in *Turbo* and *Trochus* species while they present a specific orientation in the Bi-valves examined. The Cephalopod *Nautilus pompilius* was found to have a highly symmetric arrangement of twin crystals of aragonite lying specifically oriented with respect to the lines of growth.

The results of the X-ray analysis were found to bear a close correspondence with the nature of the optical diffusion haloes observed by Sir C. V. Raman[2] in the various kinds of shells. These haloes were complete circles in the Gastropods which also gave complete rings with X-rays incident normally. The spot pattern with only one axis of symmetry corresponded

[1] S. Rama Swamy, *Proc. Ind. Acad. Sci.*, A, 1934, 1, 871–879.

[2] C. V. Raman, *Proc. Ind. Acad. Sci.*, A, 1934, 1, 859–871.

to a halo consisting of two spots and the highly symmetric spot pattern of *Nautilus* to a halo consisting of two arcs on either side.

Another interesting genus giving brilliantly iridescent shells, *viz.*, *Haliotidæ* had not been examined in the previous paper. These shells belong to the main group of Gastropods but present some differences in appearance, iridescence, etc., from *Turbo* and *Trochus*. The latter have a well-developed spiral structure while the *Haliotidæ* are flatter and more akin to the common limpet, there being only a short spire at the hinder end of the shell. It was thought interesting to investigate the nature of the arrangement of crystallites in this family of shells in order to find out whether it bears any resemblance to the previously examined Gastropods. Three different species of *Haliotis* shells were available for examination and these will be referred to in this paper as species *I*, *III* and *IV*. The first of these was the most opaque of the lot and belonged to the Californian species of *Haliotidæ* known as abalone. A photograph of this shell is given by Sir C. V. Raman[3] in part I of his series of papers on iridescent shells (Fig. 1). Species *III* was less opaque and was also a Californian variety. Species *IV* was translucent.

It was also found desirable to identify the reflecting planes corresponding to the spots in the patterns given by *Nautilus* and *M. vulgaris* in order to place the work on a quantitative basis. This involved the taking of fresh photographs in a calibrated camera and comparison with a powder pattern of aragonite taken with the same camera. The results obtained are presented and discussed.

2. *Experimental.*

The specimens cut for the present work were thinner and narrower than the previous ones in order to get much better defined X-ray diffraction patterns. The nacreous part of *Haliotis* shells consist of a number of layers of aragonite separated by layers of conchyolin which provide a sort of opaque or semi-opaque background for the iridescent colours. By mounting a piece of the shell with beeswax-rosin or canada balsam on a piece of glass plate and judicious grinding with emery powder and water, one could easily obtain single layers of this type without any conchyolin. These were more or less transparent and were of the order of about 0·1 mm. in thickness. Suitable pieces about 4 or 5 mms. long and about 0·5 mm. or less wide were cut from these, with a fine jewellers' file, while they were still mounted on glass and the pieces washed thoroughly with xylene. They were then mounted accurately in the specimen holder of a plane X-ray camera and the patterns produced were photographed. As before molybdenum K_α and K_β radiations

[3] C. V. Raman, *Proc. Ind. Acad. Sci.*, A, 1934, **1**, 567–573.

were used and with an applied kilovoltage of 50 and a tube current of about 20 milliamperes, good photographs could be obtained in about 2 hours, working with a 25 cycle supply and single wave rectification.

Two cameras were used, one of which was provided with a two-circle goniometer for carrying the specimen, while the other had a special type of specimen holder with adjusting screws for aligning and centering the specimen. The latter camera in which the specimen could be rotated during the exposure was particularly suited for taking powder patterns or other patterns for accurate comparison with each other and measurement. The first camera was used for taking photographs with various settings of the specimens. Some of the photographs obtained are reproduced in the figures illustrating this paper.

The portions of the ground sections which remained after cutting away the specimens required for X-ray examinations, were washed in xylene and mounted with canada balsam on microscope slides and covered with cover glasses. These were used for observations of the optical diffusion haloes which have been studied by Sir C. V. Raman[4] and also for microscopic examination under low power for finding out the directions of the lines of growth. Only specimens from sections of *Haliotis* which gave circular or nearly circular haloes were chosen for X-ray examination, thus ensuring that the laminations were parallel to the surface of the specimen. Thus by setting the specimen with its face perpendicular to the axis of the camera one could be sure of the X-ray beam being normal to the laminations.

In order to adjust the specimen with its face perpendicular to the axis of the camera the method given by Davey,[5] which may perhaps be briefly described here was used. The principle of the method consists in passing light through the lead slit of the camera and so adjust the specimen that the light retraces its path after reflection by it. The reflection from the specimen can be easily observed by holding a microscope cover glass inclined at about 45° to the camera axis between the slit and the source of light. When the reflected light has maximum intensity the face of the specimen will be perpendicular to the axis of the camera. Once this adjustment is made with the goniometer circles set to zero, it is an easy matter to set the specimen with its laminations inclined at definite angles with the normal position. The directions of the lines of growth in all cases except where otherwise stated are vertical in the photographs obtained.

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[4] *Loc. cit.*

[5] W. P. Davey, *A Study of Crystal Structure and its Applications*, McGraw Hill Book Company, 1934, p. 176.

Fine powder from the shells was obtained by cutting through with a fret-saw, after rubbing away the unwanted outermost layers. The powder was made to adhere nicely to a thin glass fibre, with a little diluted cellulose lacquer generally used for coating the Lindemann glass windows of X-ray tubes. This coated fibre was mounted in the second camera, centred and aligned, and rotated during the exposure. Powder photographs of calcite and aragonite were also obtained in the same way. The position of the film casette was the same in all these experiments and its distance from the specimen (47·6 mms.) was obtained from measurements of a powder pattern of analytically pure sodium chloride, as usual. The specimen to film distance in the goniometer camera was also adjusted to approximately the same value as in the second camera.

3. *Discussion of Results.*

A photograph taken with the X-rays incident normally on a thin piece of *Nautilus* is given in Fig. 2. The direction of the lines of growth is vertical in this photograph. This is similar to the corresponding photograph for *Nautilus* given in the previous paper, but was taken in the calibrated second camera mentioned earlier. Consequently, measurements of the distance of the spots from the centre and accurate comparison with powder patterns of aragonite, have been possible. The reflection planes corresponding to the spots have been found out by this means, some of which are marked in the photograph.

It is known that the *c* axis of the aragonite crystallites is normal to the shell. Consequently in a photograph taken with the X-rays normal to the shell, reflections from the planes 001 will be absent since these planes are normal to the X-ray beam. The X-ray beam will be parallel to planes 0k0 and h00 and only such of these will reflect as have their glancing angles less than the error in orientation of the *c* axis. This error is of the order of about 15°.

In Fig. 2, the reflections of the 112 plane lie on the horizontal on either side of the lines of growth. Consequently the projection of this plane normal to the *c* axis must coincide with the lines of growth. This projection is the same as that of the 110 plane across which aragonite twins. Hence the directions AB and CD in the arrangement suggested previously (Fig. 2 of earlier paper) are respectively parallel and perpendicular to the lines of growth.

The pattern of Fig. 2 can also be produced by two sets of single crystal units lying inclined at 120° to each other, that is to say, in the positions which would be occupied by the two elements of a twin crystal. There is no means of distinguishing between this arrangement and the one suggested previously. The same pattern can also be produced by one set of twins only instead

of two sets as previously suggested. But no argument can be put forward as to why the twin crystals should all be pointing one way and hence the previously suggested arrangement is the more probable one.

The error in orientation in the plane of the shell laminations as measured from the photographs is of the order of 25°. The angle between the projections of the planes 112 and 100 on the *ab* plane is about 150° in aragonite. The angular separation of the corresponding reflections, in Fig. 1, are found to be 150° by measurement.

A photograph obtained with the X-rays normal to the laminations in the nacreous layer of *M. vulgaris* is given in Fig. 1. The direction of the lines of growth in this pattern is vertical. From a comparison of this figure with that of *Nautilus pompilius* (Fig. 1) it can be easily seen that the latter is obtained by combining with the spots of the pattern of *M. vulgaris*, their images formed by a reflecting plane normal to the paper and parallel to the direction of the lines of growth. The reflections due to 100 and 112 planes are marked in the figure and by following the same line of argument as adopted for *Nautilus*, one can deduce the nature of the arrangement of aragonite crystallites.

An arrangement of the crystallites with their 110 planes along the lines of growth fits in with the nature of the pattern obtained. There is no twinning, since twinning would have produced a pattern symmetrical about the direction of the lines of growth like that of *Nautilus*. The optical diffusion halo of this shell consists of two spots as observed by Sir C. V. Raman.[6] But the line joining them is not perpendicular as mentioned in the author's previous paper, but inclined at a smaller angle than 90°. This angle may be of the order of 60°. The direction of the lines of growth was not accurately known in the previously examined section and so it was assumed that the line joining the spots may be perpendicular to the lines of growth. The fact that the crystallites are inclined to the lines of growth as in the arrangement suggested above is corroborated by this observation.

Patterns obtained with the X-rays normal to the laminations in specimens of the *Haliotis* shells consist of one complete ring and a number of arcs (Figs. 3 to 5). At first, it was thought that the presence of the arcs instead of complete rings may be due to the laminations not being exactly parallel to the faces of the specimens. For this reason one of the specimens of *Haliotis IV* was kept in the goniometer camera and inclined from its previous normal position through known angles, the axes of rotation for these settings being the vertical and the horizontal axes normal to the X-ray beam.

[6] *Loc. cit.*

The photographs obtained are given in Figs. 6 and 7, from which it is obvious that the previously set positions must have been the correct ones. In none of these settings does one get complete circles.

The patterns in Figs. 3 to 5 can all be obtained by rotating the corresponding pattern of *M. vulgaris* (Fig. 1), through angles between 60° and 90° on either side of its original position, about an axis normal to the plane of the paper. Thus the arrangement of crystals in all the species of *Haliotis* is similar to that of *Margaratifera vulgaris* with large errors of orientation between 60° and 90°. There is however one difference between the two shells. The 110 plane in *Haliotis IV* is normal to the lines of growth instead of being parallel as in *vulgaris*. The error in orientation is larger in the more opaque species than in the more transparent ones. It is nearly 90° in *Haliotis I* and *III*, and about 60° in *IV*.

Powders of all the three species of *Haliotis* gave a Debye-Scherrer ring pattern characteristic of aragonite. The diameters of the rings agreed with those given by aragonite, within the limits of errors of measurement. This may not mean that the fundamental axes of the aragonite in the shell is exactly the same as that of mineral aragonite. But if there are any differences due to distortion of the lattice, etc., they are too small for detection with a plane camera in which the specimen to plate distance is only 47·6 mms.

I have great pleasure in recording my deep appreciation of the continued interest that Sir C. V. Raman, Kt., F.R.S., N.L., has taken in this investigation and in thanking him for the same. I am very grateful to him for sparing specimens from his collection of beautiful shells for this investigation.

4. *Summary.*

X-ray diffraction patterns, obtained with monochromatic X-rays, of some species of *Haliotis* shells have been studied. It is found that the patterns given by these shells with normally incident X-rays are somewhat different to what has been previously obtained with *Turbo* and *Trochus*. In the latter shells there is random orientation of the *a* and *b* axes of aragonite crystallites. But in *Haliotis* species instead of random orientation of this type there is preferred orientation of the *a* and *b* axes with a large error in orientation. The *c* axis is normal to the laminations as in all the other aragonite shells examined previously. Patterns obtained with *Nautilus pompilius* and *M. vulgaris* have been measured and the Bragg planes causing the various reflections identified. From these measurements, the type of orientation of twin crystals of aragonite suggested for *Nautilus* in the author's previous paper is confirmed. Also the nacreous layer of *M. vulgaris* is found to consist of single crystals of aragonite with their 110 planes parallel to the lines of growth, and the *c* axis normal to the shell surface.

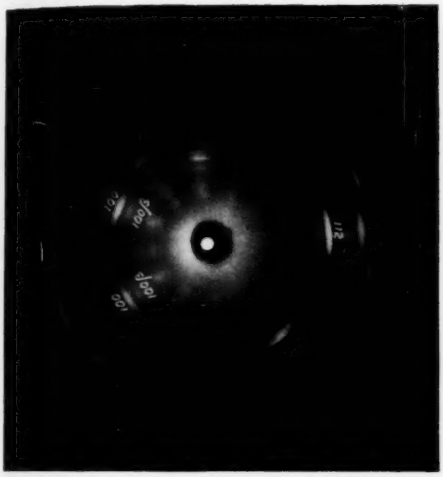

FIG. 1.

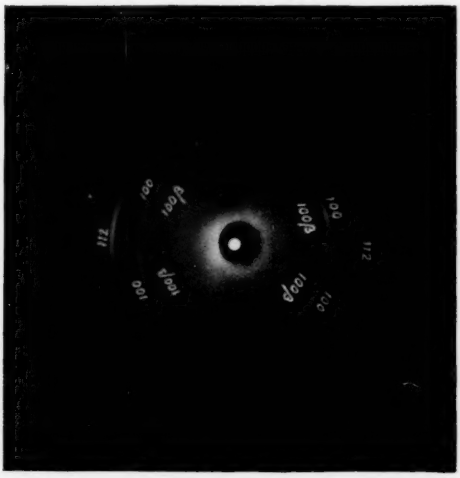

FIG. 2.

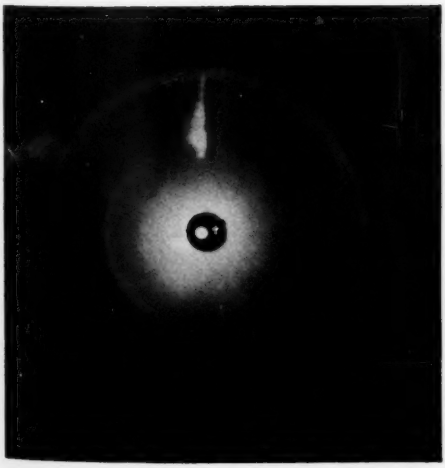

FIG. 3.

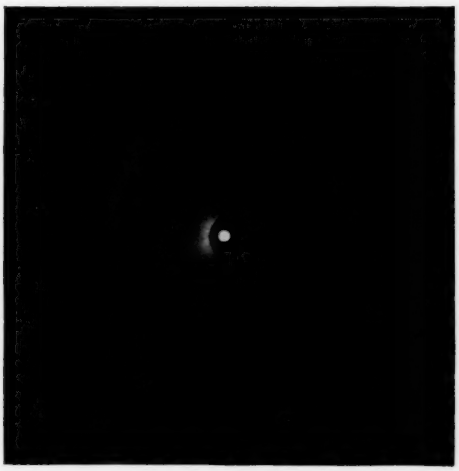

FIG. 4.

EXPLANATION OF PLATES.

FIG. 1.—*Margaratifera vulgaris*, X-rays normal to shell, lines of growth vertical.

FIG. 2.—*Nautilus pompilius*, do. do.

FIG. 3.—*Haliotis I*, X-rays normal to shell, lines of growth not known.

FIG. 4.—*Haliotis III*, do. do.

FIG. 5.—*Haliotis IV*, X-rays normal to shell, lines of growth vertical.

FIG. 6.—*Haliotis IV*, X-rays parallel to shell, lines of growth vertical.

FIG. 7.—Specimen of Fig. 5 inclined at 10° to previous position, lower end of specimen towards the camera.

FIG. 8.—*Haliotis IV*, do., lower end of specimen away from the slit of the camera.

Note.—In the previous paper by the author (*loc. cit.*), the photograph of Fig. 15 has been wrongly turned through 90° from the correct position. As it now stands, the lines of growth are therefore horizontal and not vertical as given in the explanation of plates on page 879 in the previous paper.

THE FLAME SPECTRA OF SOME AROMATIC COMPOUNDS.

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Received September 12, 1935.
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introductory.

The study of the spectra of flames is of interest not only from the point of band-spectroscopy but also from the chemical standpoint as these throw light on the mechanism of combustion. In an earlier paper by the author,[1] a band-system which had previously received little attention was fully described: it had appeared with great intensity in the inner cone of the flame of ethylene, burning in air in a Smithells' flame-separator. These bands were provisionally attributed to HCO mainly on three grounds:— (1) The separation of successive bands in their vibrational analysis did not show any relationship to any of the known separations in the spectra of C_2, CH and HO which accompany the new bands in the ethylene flame, nor to those of CO, or of formaldehyde. (2) The constants in the formula representing the bands in question had a striking resemblance to those of the β-bands of NO. If they were assumed to originate in HCO, this similarity could be explained on Mecke's principle of isosterism. (3) The presence and great intensity of the bands particularly in ethylene could be accounted for by supposing that in the process of combustion the O_2 molecule entered the ethylene molecule and breaking the double bond in it formed two HCO groups—a conclusion important from the point of view of the mechanism of combustion. This supposition of the direct incorporation of the O_2 molecule in a hydrocarbon molecule received additional support from a study of the spectra of other flames of aliphatic carbon compounds which the author had carried out in Professor A. Fowler's laboratory. Full details will be published in due course but the main facts may be referred to here briefly.

The inner cone of the flame of acetylene which has a triple bond gave the HCO bands though not with as great an intensity as with ethylene. The triple bond makes the molecule unstable and in consequence a great

[1] W. M. Vaidya, *Proc. Roy. Soc.*, 1934, **147A**, 513.

intensity of the HCO bands could hardly be expected. The inner cone of the methane flame also yielded the HCO bands, somewhat faintly : the four bonds of carbon are satisfied and hence the entry of the O_2 molecule in methane would be difficult and thus but few HCO groups would be formed. The same reasoning applies to the explanation of the spectra of the inner cones of methyl chloride and acetaldehyde which exhibited the HCO bands. These four flames also showed the C_2, CH and HO bands in addition to the HCO bands referred to above.

The complete absence of the HCO bands from the spectra of the flames of formaldehyde, formic acid and methyl alcohol was also noticed and appeared to be significant. The C_2 bands were also absent from the spectra of the flames of formaldehyde, formic acid and methyl alcohol ; the CH bands were present in the spectrum of methyl alcohol but not in that of formaldehyde or of formic acid. All these latter three flames exhibited the CO flame bands and the HO bands.

Since the investigation of the spectra of flames of aliphatic carbon compounds had thus proved to be of great interest, it was considered desirable to extend spectroscopic observations to flames of the aromatic series. Such an investigation has now been carried out by the author in Sir C. V. Raman's laboratory and the results are embodied in the present paper.

In this connection, the spectra of the flames of (1) benzene, (2) toluene, (3) phenol, (4) resorcinol, (5) pyrogallol, (6) benzaldehyde, (7) benzoic acid, (8) aniline, (9) nitrobenzene, (10) pyridine, and (11) diphenyl oxide, were studied.

Photographs of the spectra were taken with one of Hilger's small quartz spectrographs (E 31). The use of such an instrument, though of a small dispersion, results in a great saving of time which in the case of flames is a serious problem on account of the extreme faintness of their spectra and the difficulty of maintaining the flames for any length of time. All the bands occurring in their spectra are known, so that no measurements were necessary. Ilford's Golden Iso-Zenith plates were used.

2. *Details of the Flame Technique.*

In the cases of benzene and toluene, the two liquids were slightly warmed in a distilling flask and air under small pressure was bubbled through them by means of an electrical blower. The vapours were ignited on the top of a micro-burner. With its air-hole closed the flames were smoky and luminous with small greenish inner cones. On opening the air-hole, they became non-luminous and developed well-marked inner cones. No attempt towards the complete separation of the cones by means of a flame-separator was made because in the author's experiments with aliphatic

flames no advantage accrued by such separation as far as the spectra were concerned except in the case of ethylene.

The method of bubbling air through the substance was unsuitable for the production of the flames of the remaining compounds because some of them were solids and some had to be heated to a rather high temperature which resulted in their condensation at the micro-burner. Phenol, resorcinol, pyrogallol and benzoic acid were therefore melted in a wide pyrex tube one end of which was sealed and the other drawn to a narrow neck. An asbestos wick dipping in them was sufficient to give their flames. Similarly a continuous flame was obtained by using an asbestos wick with benzaldehyde, aniline, nitrobenzene and pyridine all of whom had to be slightly warmed up. No heating was necessary for diphenyl oxide.

The flames in all cases were extremely luminous and smoky, depositing a considerable amount of soot which was diminished by blowing air on the top part of the flames. Just at their bases, however, there were a few greenish spots, which when focussed on the slit of the spectroscope gave the spectra described below.

3. *Description of the Spectra.*

The HCO bands were obtained in the spectra of all the flames studied. They were of both the A and B types. As described in the paper on ethylene, the B bands appeared when its flame was modified, but in the aromatic flames they were given without any modification of the original flames. A similar appearance of the B bands in the natural state of a flame was found in the inner cones of ether and ethyl alcohol.

The intensity of the HCO bands, however, varies from flame to flame. They are fairly strong in toluene, phenol (Plate XIX*b*) and diphenyl oxide (Plate XX*a*) though not comparable with ethylene, and they are faint in the spectra of the remaining substances.

The inner cones of all compounds had the C_2, CH and HO bands.

4. *Appearance of CN and NO Bands.*

One interesting feature of the spectra of aromatic compounds was the occurrence of the CN bands and of the γ bands of NO in the flames of aniline (Plate XX*b*), nitrobenzene and pyridine (Plate XX*c*). It had been previously noticed that they appeared in acetylene and this was explained on the supposition that the high temperature of the acetylene flame brought about the activation of atmospheric nitrogen. On the other hand, in the spectra of aniline, pyridine and nitrobenzene, the nitrogen forming a constituent part of their molecules was evidently responsible for the CN and NO bands. The CN bands were more intense than the NO bands and with their appearance the CH bands diminished in intensity.

5. Comparison of Aliphatic and Aromatic Flame-Spectra.

(1) Aromatic flames are far more smoky than aliphatics.

(2) All aromatic flames included in the present investigation gave the HCO bands which appeared only in some flames of the aliphatic series. Moreover, the HCO bands in the aromatic substances were of both the A and B types—no modification of the original flames was necessary for the appearance of the B bands. In aliphatic flames, only ether and ethyl alcohol yielded the B bands while burning naturally while the flame of ethylene had to be modified for their appearance.

(3) In the aliphatic compounds, there was a gradual variation of spectra from one substance to another. Thus formaldehyde and formic acid gave the HO and the CO flame bands; methyl alcohol had the HO and the CO flame bands and in addition those of CH. From these three flames, the HCO and the C_2 bands were absent. The HCO and the C_2 bands were however present in the spectrum of methane and also CH and HO, but not CO flame bands. In the aromatic flames, however, there is more uniformity, all flames giving the C_2, CH, HO and HCO bands.

TABLE I.

Intensity of the Bands.

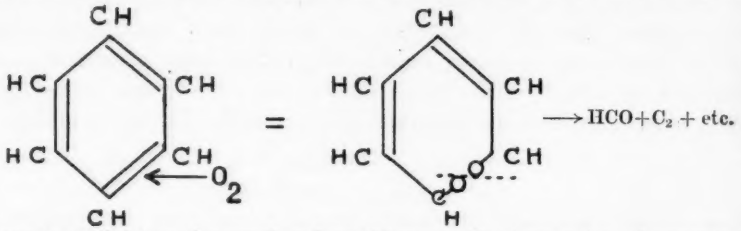
Nature of flame	C_2	CH	HO	HCO A and B	CN	γ bands of NO	Reference to plates
Benzene (C_6H_6)	4	5	3	0·5	..	..	XIX*a*
Toluene ($C_6H_5CH_3$) ..	4	5	4	1·0	..	..	
Phenol (C_6H_5OH) ..	4	5	3	0·9	..	..	XIX*b*
Resorcinol [$C_6H_4(OH)_2$] ..	2	3	2	0·4	..	..	
Pyrogallol [$C_6H_3(OH)_3$] ..	1·8	3	2	0·3	..	..	XIX*c*
Benzaldehyde (C_6H_5CHO) .	2	3	2	0·6	..	..	XIX*d*
Benzoic acid (C_6H_5COOH) ·	2	3	2	0·5	..	..	
Diphenyl oxide $C_6H_5OC_6H_5$	2	3	2	0·9	..	..	XX*a*
Aniline ($C_6H_5NH_2$) ..	1·2	1·5	1·2	0·3	4	2	XX*b*
Nitrobenzene ($C_6H_5NO_2$) ..	1·2	1·5	1·2	0·3	4	2	
Pyridine (C_5H_5N) ..	1·2	1·5	1·2	0·5	4	2	XX*c*

(4) In the CH_4 flame, the intensity of the C_2 bands was specially very susceptible to the oxygen supply; in C_6H_6 the intensity of the C_2 bands seemed independent of the quantity of oxygen mixed with it.

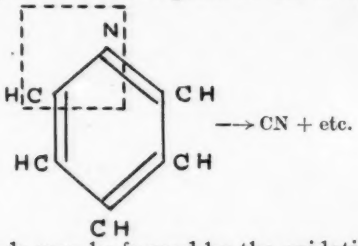
For helping in the discussion of the results, the spectra of the flames investigated are quantitatively characterised in Table I. The figures refer to the eye estimates of the intensities of the various bands occurring in the individual flames.

6. Discussion.

The existence of the HCO bands in all the aromatic compounds investigated may reasonably be explained as due to the double bond in them and the decomposition of oxygenated molecules formed by the direct incorporation of the O_2 molecule in the benzene ring. The O_2 molecule must be assumed to enter the ring at one of the double bonds as in ethylene.

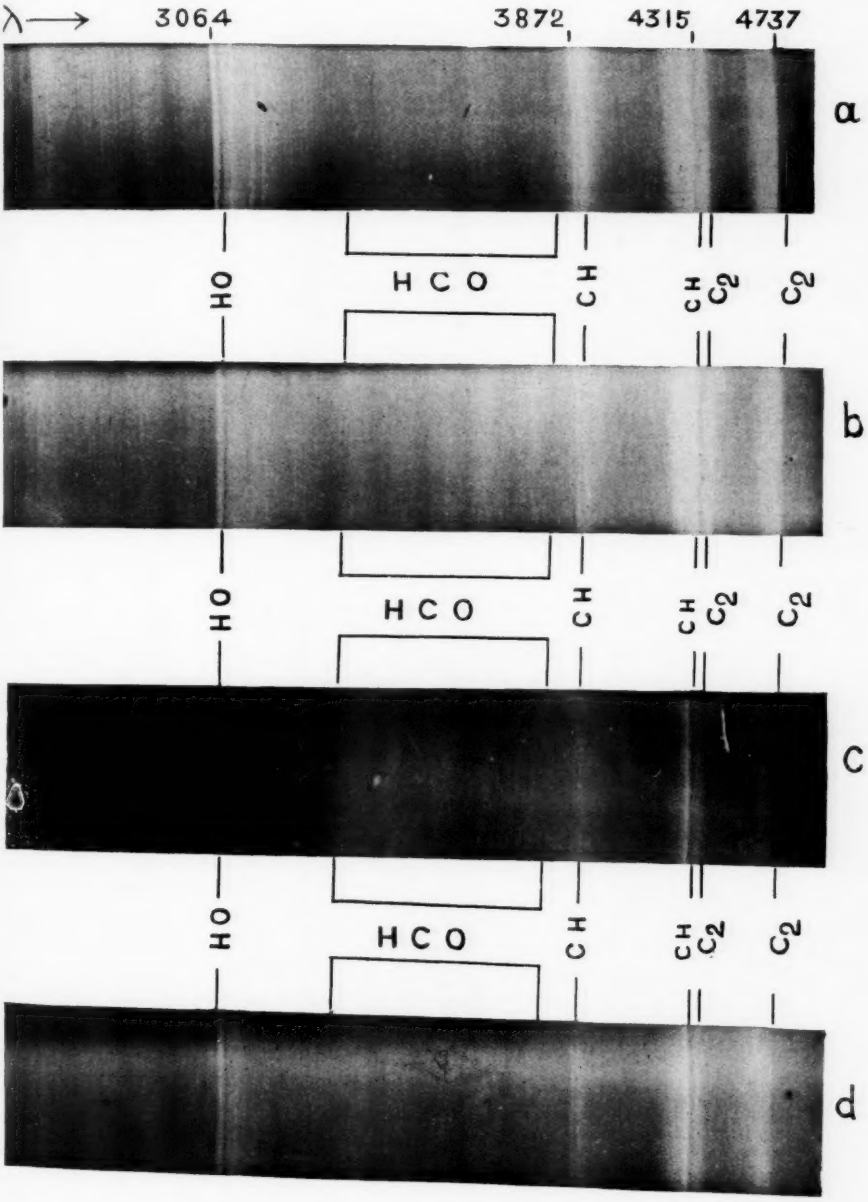


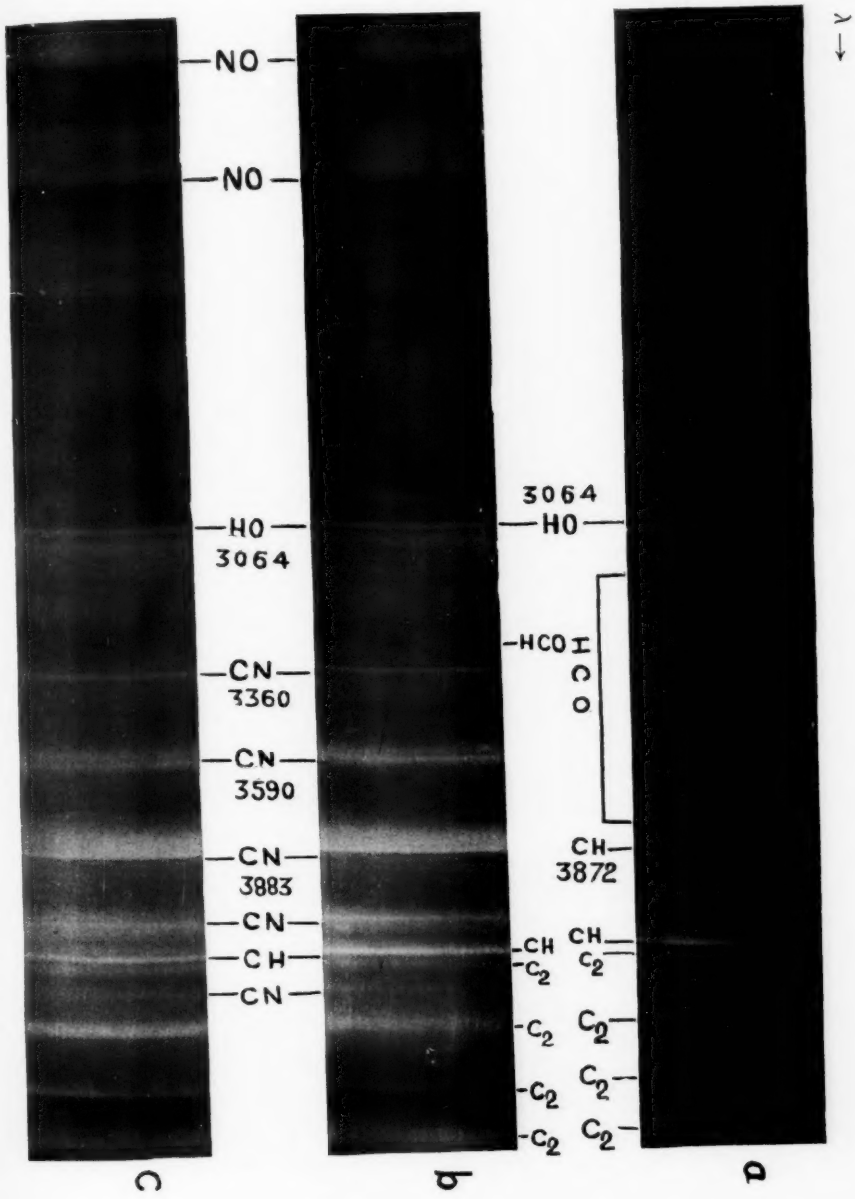
Important light on the combustion of benzene is thrown by the spectrum of pyridine. Its spectrum includes the CN and NO bands, the intensity of the CN bands being greater than that of NO or CH. The breaking up of the benzene ring seems to take place at the N atom.



The NO bands may be formed by the oxidation of N in the ring or the subsequent reaction of CN with the atmospheric oxygen. The rupture of the ring at N producing CN seems a more favoured reaction than the simple oxidation of N forming NO because of the great intensity of the CN bands compared with NO.

If it be supposed that the oxidation of benzene proceeds through the successive formation of hydroxyl groups, as might happen according to "the hydroxylation theory" of combustion, spectra of C_6H_6, C_6H_5OH, $C_6H_4(OH)_2$ and $C_6H_3(OH)_3$ should differ from one another but the observed spectra show


λ⟶
3064
3872
4315
4737
a
HO
HCO
CH
CH
C2
C2
b
HO
HCO
CH
CH
C2
C2
c
HO
HCO
CH
CH
C2
C2
d


NO
NO
HO
3064
CN
3360
CN
3590
CN
3883
CN
CH
CN
3064
HO
HCO
I
O
O
CH
3872
CH
C2
C2
C2
C2
C2
C2
C2
C
b
a
λ

that the spectrum of pyrogallol with three (OH) groups is not different from that of benzene with no (OH) group at all. Hence the hypothesis of successive formations of (OH) groups does not seem to work well in the benzene oxidation.

A complete scheme for the combustion of benzene cannot yet be given because little information about the subsequent reactions between the free radicals like CH, HO, C_2, CN, NO, etc., is available.

In conclusion the author wishes to express his sincere thanks to Sir C. V. Raman for his kind permission to work in his laboratory. The author is also grateful to him for the grant of a scholarship.

7. *Summary.*

The author's previous investigation of the spectrum of the flame of ethylene burning in a Smithells' flame-separator proved to be of great interest because it led to the appearance with great intensity of a band system which had hitherto received little attention. There were reasons to believe that it was due to HCO. One of the arguments in favour of HCO as the emitter of this band system was that the O_2 molecule might be supposed to be directly incorporated in the ethylene molecule and breaking the double bond formed two HCO groups, thus accounting for the great intensity of the HCO bands particularly in ethylene. This hypothesis of the direct incorporation of the O_2 molecule received additional support from the study of the spectra of other aliphatic carbon compounds.

A similar investigation of the aromatic flames was undertaken and the results of a study of the spectra of eleven flames are given in the paper.

The bands attributed to HCO were also found to occur in the spectra of the flames of benzene and other aromatic compounds. Their appearance in the aromatic flames has been explained as due to the double bond of the benzene ring and the breaking up of oxygenated molecules formed by the direct incorporation of the O_2 molecule.

The spectra of aliphatic and aromatic flames are compared. There is a gradual variation in the spectra of the flames of aliphatic series, while there is more uniformity in the spectra of benzene and its related compounds.

Considerable light on the mechanism of combustion of benzene is thrown by the spectra for pyridine, aniline and nitrobenzene in which flames the CN bands and the γ bands of NO appeared. The rupture of the ring seems to take place at the N atom.

A tentative scheme for the combustion of benzene is given ; it is however incomplete for want of knowledge of subsequent reactions between free radicals like CH, O_2, CN, NO, etc. But the hypothesis of the direct incorporation of the O_2 molecule explains the spectroscopic observations better than that of successive formation of hydroxyl groups.

LIGHT SCATTERING IN GOLD SOLS IN RELATION TO PARTICLE SIZE AND SHAPE.

By D. S. Subbaramaiya.
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Received September 21, 1935.
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. Introduction.

The determination of the condition of the colloid particle and especially its size, shape and structure is one of the most important problems in the physics of the colloidal state. The study of the Tyndall effect is obviously one of the most fruitful methods that can be employed to resolve this problem. In an earlier paper by the author,[1] the depolarisation of the Tyndall scattering in a number of typical colloids was reported on and the importance was emphasised of measuring the three values, namely, ρ_U, ρ_V and ρ_H of the depolarisation of the transversely scattered light referring respectively to the cases in which (*a*) the incident light is unpolarised, (*b*) it is polarised with its electric vector perpendicular to the direction of observation, (*c*) parallel to the direction of observation. The values of the three quantities, both absolutely and relating to each other, are very significant as indicators of the size, the shape and the structure of the particles. The value of ρ_V by itself is an indicator of the anisotropy of shape or structure of the particles, while the value of ρ_H is specially sensitive to the size of the particles. R. S. Krishnan[2] has shown by an application of the theorem of reciprocity that the three quantities ρ are connected by the relation

$$\rho_U = \frac{1+1/\rho_H}{1+1/\rho_V} \quad .. \quad .. \quad .. \quad .. \quad .. \quad \text{(A)}$$

which takes the special form

$$\rho_U = \frac{2\rho_V}{1+\rho_V} \quad .. \quad .. \quad .. \quad .. \quad .. \quad .. \quad \text{(B)}$$

in the special case when the particles are exceedingly small, ρ_H then becoming unity. It appeared of importance to investigate the relative values of ρ_U, ρ_V and ρ_H in the classical case of gold sols, the study of which, as is well known, played an important part in the history of the development of colloid science.

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[1] D. S. Subbaramaiya, *Proc. Ind. Acad. Sci.*, A, 1935, 1, 710.
[2] R. S. Krishnan, *Proc. Ind. Acad. Sci.*, A, 1935, 1, 783.

2. *Previous Work on Gold Sols.*

Among the various investigators that have made a study of the phenomena exhibited by gold sols, mention must be made of Mie,[3] Steubing,[4] Lange,[5] Diesselhörst and Fruendlich[6] and Bjornstähl.[7] Mie has developed formulæ for the absorption and the scattering of light in colloids, assuming that the particles are spherical in shape. Steubing has shown experimentally that in gold sols, the transversely scattered light is not completely polarised, even when the incident light is plane polarised. From considerations based on Steubing's experimental results and his own theoretical calculations, Mie concludes that the particles in gold sols are not strictly spherical in shape though the other optical properties of these sols, such as the absorption of light, can be satisfactorily explained on the supposition that they are spherical. Subsequently, Lange has made detailed investigations of the absorption and the scattering of light in gold sols. The large depolarisations of the light scattered transversely by the sols indicate that the particles are in the form of rods or discs while the absorption measurements are strictly in accordance with Mie's theory indicating that the particles are spherical in shape. To solve this contradiction, Lange postulates that a large fraction of the particles in the sols are spherical in shape and these manifest themselves in absorption measurements and a small fraction of the particles are rods or discs and these cause the observed partial polarisation of the Tyndall light.

Diesselhörst and Fruendlich have considered the effects of the flow of colloids on the light absorption and the Tyndall scattering in them. According to them, colloids containing non-spherical particles bring about changes in these phenomena during their flow, but those containing spherical particles do not. The experiments showed that the particles in gold sols could be treated as spherical.

Bjornstähl has made a study of the accidental double refraction in colloids. Gold colloids made by using nuclear sols and hydrogen peroxide as the reducing agent showed magnetic, electric and streaming double refraction. Those prepared by various other methods did not show any effect. A sample of gold colloid, made by using ferrous sulphate as the reducing agent, showed negative double refraction in a magnetic field. While this

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[3] G. Mie, *Ann. der Phys.*, 1908, **25**, 377.

[4] Steubing, *Ann. der Phys.*, 1908, **26**, 329.

[5] Lange, *Zeit. f. Phys. Chem.*, 1928, **132**, 27.

[6] Diesselhörst and Fruendlich, *Phys. Zeit.*, 1916, **17**, 117.

[7] Bjornstähl, *Inaugural Dissertation, Uppsala*, 1924.

last result may be regarded as being due to the presence of small traces of iron, it is difficult to understand why the sols made by using hydrogen peroxide as the reducing agent should show accidental double refraction. The results are surprising and the subject demands careful investigation.

In view of all this it was thought necessary to undertake a study of the optical and the magnetic properties of colloids in order to find out their true physical nature. A fresh investigation of the depolarisation of the Tyndall scattering in gold sols, in the light of the new methods already indicated, has been made. While Lange has confined his attention to the measurements of ρ_U alone, the measurements of ρ_V and ρ_H have also been made. That the value of ρ_U depends on wave-length has been shown experimentally by Lange. The measurements reported in this paper have all been carried out with incident white light. The dependence of ρ_U, ρ_V and ρ_H on wave-length is being investigated and the results obtained will be published in a separate communication.

3. Preparation of Gold Sols.

In order to obtain clear, good and stable sols, the necessary precautions were taken. All the vessels used were of resistance glass and they were first cleaned thoroughly with hot chromic acid and then well steamed. The necessary reagents and other solutions were prepared using double distilled water. Six different sols were made. Two were prepared according to the method employed by Faraday (I and II). Three were prepared according to the nuclear method, using hydrogen peroxide as the reducing agent. This was the method employed by Bjornstähl for the preparation of his sols which showed accidental double-refraction. The nuclear sol used in all these cases was Faraday's sol I. Another sol was made by the method given by Zsigmondy (VI). All these sols are preserved in resistance glass bottles, thoroughly cleaned and well steamed.

I. The method of Faraday for the production of colloidal gold consists in the use of a solution of phosphorus in an organic liquid as the reducing agent. A sol was made by adding 2·5 c.c. of a ·6% chlorauric acid and 3 c.c. of ·18 N potassium carbonate to 120 c.c. of pure double-distilled water followed by the addition of 1 c.c. of a pure ether solution of phosphorus prepared by diluting the saturated solution with five times its volume of ether. In the cold the mixture changed to a brown colour, which gradually became red, the reaction being complete in about 60 hours.

II. Another sample of a gold colloid was made exactly on the same lines as I, but the reaction being rendered almost instantaneous by boiling the mixture. A clear red sol resulted.

III. 2 c.c. of a ·6% chlorauric acid were added to 100 c.c. of pure double-distilled water. 4 c.c. of the nuclear sol were added followed by the addition of a few drops of a very dilute solution of hydrogen peroxide. A clear red sol formed immediately.

IV. Another sample was made using the same method as that in III except that the mixture was kept boiling while the reducing agent was added. This was also a clear red sol.

V. Yet another sample was made. In this case the mixture was kept boiling and 6 c.c. of ·18 N potassium carbonate solution were added and then the reducing agent. The sol obtained was clear and deep-red in colour.

VI. A blue sol was obtained as a result of employing a method of preparation suggested by Zsigmondy. 2 c.c. of ·6% chlorauric acid were added to 100 c.c. of pure double-distilled water followed by 6 c.c. of ·18 N potassium carbonate solution. The mixture was then heated to boiling and 4 c.c. of the nuclear sol were added followed by 5 c.c. of a ·03% solution of formaldehyde drop by drop. The sol which resulted was boiled and it turned blue.

4. Experimental Results.

The experiments were made within a dark cabin into which sunlight was reflected by a single mirror Foucault Heliostat. A Dallmeyer photographic lens of adjustable aperture and focal length 1 foot fixed to the wall of the cabin served to bring the sunlight to a focus, at the centre of a rectangular glass cell containing water in which was immersed the bottle containing the sol. The rectangular glass cell itself was placed in a wooden box painted dull-black on the inside, having three openings, two for the entry and exit of the incident beam of light and the third for the observation of the scattered light exactly opposite the focus of the track in the disperse system. The wooden-box was mounted on a stand capable of being raised or lowered. The incident beam could be polarised in any plane by means of a nicol suitably mounted. The following measurements (expressed as percentages) were made:

	Red Sols					Blue Sol
	I	II	III	IV	V	VI
ρ_V ..	7·7	17·2	10·5	10·6	9·4	9·9
ρ_H ..	100	100	96·5	84	96·5	54·8
ρ_U (observed)	14·5	29·5	19·8	21·7	16·9	23·3
ρ_U calculated from formula A	14·3	29·2	19·4	21	17·5	25·5
ρ_U calculated from formula B	14·3	29·2	19·1	19	17·2	19·2

From the table we observe that in the blue sol, the value of ρ_H is relatively small. Thus in this case, we are able to infer from depolarisation measurements alone, that we are dealing with particles which are relatively large. Amongst the red sols we find that ρ_H has its maximum value unity in the case of I and II and differs from it to a small or large extent in the case of III, IV and V. Also it was observed that the intensities of scattering in I and II were far smaller as compared with those in III, IV and V. These indicate that the particles in I and II are much smaller in size than those in III, IV or V. Out of the last three, the value of ρ_H in IV deviates more from unity than that in III or V, indicating that the gold particles in IV are relatively much larger in size as compared with those in III or V.

In order to confirm the conclusions drawn from the depolarisation values, observations were made by the "method of two double-image prisms".[8] In this case we observe four images, V_V, V_H, H_V, H_H. In the case of the red sol IV and the blue sol VI, H_H was definitely stronger than H_U $(=V_H)$. In the case of I, II, III and V, it was found that $H_H = H_V = V_H$. The small differences between the values of ρ_U as calculated from A and B and observed, in the case of III and V, may be due to the unavoidable errors introduced by the glass bottles and the like. In the case of the blue sol the vertical component of the scattered light had a reddish tinge and the horizontal component had an yellowish tinge. This rendered the matching of the intensities of the two tracks very difficult.

The large values of ρ_V in all cases indicate that we are dealing with particles whose shapes depart greatly from the condition of sphericity. That an increase in the rate of growth brought about by temperature results in an increase in the anisotropy is shown strikingly by the values of ρ_V in I and II. By increasing the rate of growth the particles are also made larger as is shown by the values for III and IV. A comparison of III, IV and V indicates that the effect of potassium carbonate is to diminish the anisotropy and prevent the formation of very large particles.

In conclusion, it is my pleasant duty to express my heart-felt thanks to my professor, Sir C. V. Raman, for his kind encouragement and inspiring guidance.

Summary.

Previous work on gold sols with reference to the shape of the particle has been briefly recounted. Results of the measurements of the depolarisation of Tyndall scattering corresponding to the incident light being (*a*) unpolarised, (*b*) plane polarised with its electric vector perpendicular to the plane of

[8] R. S. Krishnan, *Loc. cit.*

observation, (*c*) plane polarised with its electric vector parallel to the plane of observation, have been reported. The values obtained and the observations made indicate that the particles in Faraday's sols are much smaller as compared with those in the other red sols prepared by using nuclear sols and hydrogen peroxide as the reducing agent; those in the blue sols are relatively the largest. In all the sols examined the shapes of the particles are far from being spherical. In general the size and the anisotropy of the particles appear to increase with the increase in the rate of growth brought about by enhancing the temperature during the preparation of the sol. The addition of potassium carbonate to the mixture before reduction seems to have the reverse effect.

DIELECTRIC COEFFICIENTS OF VOLATILE COMPOUNDS OF FLUORINE AND BORON.

Carbon Tetrafluoride, Nitrogen Trifluoride, Fluoroform, Carbon-Nitrogen Compound of Fluorine $(CF_3N)_2$, Boron Hexahydride, and Nitrogenous Boron Hydride $B_3N_3H_6$.

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The chemistry of fluorine and boron compounds are of considerable interest from the valency and structural points of view. It was therefore desired to study the electrical and optical properties of some of these compounds available in the pure gaseous state. On a request made through Prof. Sir C. V. Raman, pure specimens of carbon tetrafluoride, fluoroform, nitrogen trifluoride and a new compound of carbon and fluorine with nitrogen $(CF_3N)_2$, were kindly presented by Professor Dr. Otto Ruff, who has worked extensively on the chemistry of fluorine compounds. On a similar request, pure specimens of diborane and nitrogenous boron hydride were kindly presented by Professor Dr. Alfred Stock, who has specialised in the field of boron and silicon chemistry.

The apparatus, method of measurement, and procedure adopted were the same as described in the earlier papers published in collaboration with Professor H. E. Watson.[1] Simultaneous measurements of refractive indices and dispersions were made on the same specimens of gases and the results obtained will be given in a separate communication.

Among the gases mentioned, nitrogen trifluoride, fluoroform and the new compound $(CF_3N)_2$ have finite electric moments. When the investigations on nitrogenous boron hydride $B_3N_3H_6$ were taken up (after an unfortunate delay), it was found that a considerable fraction of it had crystallised out and thus the quantity actually available for the measurements was rather small. However as careful measurements as possible were carried out with the quantity available. The results given for this compound require further confirmation.

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[1] H. E. Watson, G. Gundu Rao and K. L. Ramaswamy, *Proc. Roy. Soc., A,* 1931, **132**, 569; *ibid.,* 1934, **143**, 558.

As a check on the calibrations of the condensers, measurements of dielectric coefficients at different temperatures were carried out with freshly prepared pure carbon dioxide. The results are given in Table I.

TABLE I.

Dielectric coefficients of carbon dioxide at 760 mm. and 25°.

No.	Temperature °C.	$p_1 - p_2$ mm.	p mean	No. of readings	E—1 (uncorr.)	$E-1_{p=0}$	Remarks
1	22·9	637·6	430	5	910·0	904·8	
2	,,	637·2	,,	,,	906·7	901·5	Refractionated.
3	23·0	613·7	410	,,	906·5	901·6	
4	,,	613·5	,,	,,	906·1	901·2	
5	95·2	661·8	436	6	902·5	900·8	
6	95·4	661·7	,,	7	902·9	901·2	
7	−79·8	503·5	352	5	921·6	901·1	
8*a*	,,	252·0	480	6	929·1	901·0	
8*b*	,,	251·7	226	,,	912·4	899·4	
8*c*	,,	503·7	352	,,	921·7	901·2	No incondensible fraction.
9	,,	503·9	,,	5	921·7	901·2	

The mean values at 25°, 95° and 80° are respectively 901·4, 901·0 and 901·0. The slightly higher value at 25° is within the limits of experimental error. It may be mentioned that this value 901·0 agrees exactly with the figure given in an earlier communication.[2]

Preparation of Materials.

All the gases were purified by careful fractional distillation at low pressures and the purity of the different fractions was followed by comparing their refractive indices for white light. Identity of refractive index was taken as the criterion of purity.

Carbon tetrafluoride was condensed in a bulb at liquid air temperature and one to two bubbles of incondensible fraction were removed. The gas was then evaporated and cooled in quick succession and any traces of

[2] H. E. Watson, G. Gundu Rao and K. L. Ramaswamy, *Proc. Roy. Soc.*, 1934, **143**, 558.

dissolved incondensible impurity present was simultaneously pumped off. It was then collected at a constant vapour pressure of 50 mm. into four separate fractions over mercury. The refractive index for white light of the first and the fourth fractions differed by 1 part in 1530. These fractions were therefore mixed and refractionated and the intermediate fraction was used in the measurements.

Nitrogen trifluoride.—No trace of any fraction incondensible in liquid air was present. The gas was refractionated at a constant vapour pressure of 18 mm. The difference in refractive indices of the first and the fourth fractions was indistinguishable, indicating a high order of purity.

Fluoroform.—A trace of incondensible fraction at liquid air temperature was first removed. It was then collected at a constant vapour pressure of 50 mm. into five different fractions. A condensible impurity, which when warmed to room temperature amounted to about 1 c.c., was rejected. The refractive indices of the first and the fourth fractions were identical.

Nitrogenous fluorine compound of carbon $(CF_3N)_2$.—A trace of incondensible fraction at liquid air temperature was first removed and the gas then fractionated at a steady vapour pressure of 40 mm. A residue, which when warmed to room temperature measured about 4 c.c., was rejected. The refractive index of fractions 1 and 3 differed by 3 parts in 1780. The gas was therefore refractionated and the intermediate fractions were mixed and used in the measurements.

Diborane B_2H_6.—When condensed in liquid air, it was found that the gas had decomposed considerably. About 25 c.c. of incondensible fraction in a total volume of 100 c.c. of the original pure gas, was removed. It was then fractionated at 70 mm. steady vapour pressure. A condensible impurity, which when warmed to room temperature measured about 1·5 c.c., was removed separately. The difference in refractive index of the second and fourth fractions was negligible. The fractions 2, 3 and 4 were mixed, refractionated at low pressures and were used for the measurements.

Nitrogenous boron hydride $B_3N_3H_6$.—This compound is a liquid at ordinary temperatures and boils at 53° according to A. Stock.[3] The available quantity was condensed at solid carbon dioxide temperature. About 50 c.c. of incondensible gas was removed. The residue was then vapourised and the measurements taken.

Results.

The values of dielectric coefficients are given in Table II. The pressures are given to the nearest figure in the first decimal place though actually

[3] A. Stock, *Hydrides of Boron and Silicon*, 1933.

read correct to 0·05 mm. and the temperatures are given correct to 0°·1 C. Column (1) gives the serial number of the experiment, (2) the actual temperature in degrees centigrade, (3) the range of pressure in millimeters, (4) the mean pressure in each experiment, (5) the number of individual readings in each measurement, (6) the value of E—1 at 25°

TABLE II.

Dielectric coefficients reduced to 760 *mm. and* 25° *C.*

No.	Temp. °C.	$p_1 - p_2$ mm.	p mean	No. of readings	E−1	$E-1_{p=0}$	Remarks
			Carbon tetrafluoride.				
1	27·1	689·5	468	5	1199	1189	No incondensible fraction.
2*a*	,,	343·5	641	4	1196	1183	
2*b*	,,	,,	295	,,	1204	1198	
3	,,	687·0	467	,,	1198	1188	
4	27·2	684·7	465	5	1198	1188	
5	*95·2*	698·1	466	,,	1200	*1197*	A little incondensible fraction removed.
6*a*	,,	345·5	645	4	1203	*1198*	
6*b*	,,	353·4	293	,,	1199	*1197*	
7	,,	698·9	466	,,	1201	*1198*	
8	,,	698·7	,,	5	1198	*1195*	
9	*−79·8*	661·3	475	4	1217	*1191*	
10*a*	,,	337·6	639	5	1228	*1193*	
10*b*	,,	324·1	306	,,	1210	*1193*	
11	,,	661·7	474	,,	1219	*1193*	
12	,,	661·6	475	6	1219	*1193*	
13	26·4	656·7	444	5	1201	1191	
14	26·5	656·2	,,	,,	1203	1193	

TABLE II—(*contd.*)

No.	Temp. °C.	$p_1 - p_2$ mm.	p mean	No. of readings.	E−1	E−1$_{p=0}$	Remarks
			Nitrogen trifluoride.				
1	25·6	660·6	449	5	1228	1218	
2*a*	,,	321·8	621	,,	1230	1217	
2*b*	,,	338·6	288	,,	1226	1220	
3	,,	660·4	449	,,	1228	1218	
4	,,	660·5	,,	,,	1228	1218	
5	95·0	706·4	474	,,	*1205*	*1202*	
6*a*	,,	360·4	649	,,	*1207*	*1202*	
6*b*	,,	345·5	294	,,	*1206*	*1204*	
7	,,	706·0	474	,,	*1205*	*1202*	
8	*94·8*	704·4	472	6	*1207*	*1204*	
9	*−79·8*	671·5	481	,,	*1320*	*1287*	No incondensible fraction.
10*a*	,,	350·5	644	7	*1332*	*1287*	
10*b*	,,	320·8	306	6	*1309*	*1288*	
11	,,	671·3	482	7	*1320*	*1287*	
12	,,	672·1	,,	6	*1318*	*1285*	
13	28·5	669·2	453	5	1230	1220	
14	28·4	669·0	,,	,,	1230	1220	
15	28·3	515·4	342	,,	1229	1222	
16	23·3	646·1	416	,,	1228	1219	Refractionated twice.
17	,,	646·0	,,	,,	1229	1220	

and 760 mm. pressure calculated on the assumption that the gas is ideal, (7) the values corrected for compressibility. In the last column is mentioned any treatment given to the gas during the course of measurements. E−1 in the table stands for $E-1^{760\ mm.}_{25°} \times 10^6$.

TABLE II—(*contd.*)

No.	Temp. °C.	$p_1 - p_2$ mm.	p mean	No. of readings.	E−1	E−1$_{p=0}$	Remarks
				Fluoroform.			
1	27·2	226·3	146	5	7478	7456	
2	27·3	,,	,,	,,	7480	7458	
3	*95·2*	248·4	157	,,	*6291*	*6284*	
4	,,	248·2	,,	,,	*6289*	*6282*	
5	,,	343·4	219	6	*6281*	*6272*	More gas introduced.
6	*−79·8*	113·3	76	5	*11065*	*10988*	No incondensible fraction.
7*a*	,,	59·1	104	,,	*11085*	*10978*	
7*b*	,,	54·1	47	4	*11244*	*11195*	
8	,,	113·4	76	5	*11075*	*10998*	
9	,,	113·7	,,	,,	*11055*	*10978*	
10	30·6	228·9	147	5	7397	7375	No incondensible fraction.
11	30·4	227·9	146	,,	7400	7378	
12	23·3	264·2	169	6	7559	7533	Refractionated. Dispersion repeated.
13	23·4	211·8	135	5	7549	7528	
14	*95·0*	268·9	169	,,	*6269*	*6262*	
15	,,	269·0	,,	6	*6269*	*6262*	
16	*−79·8*	129·1	86	4	*11095*	*11007*	
17	,,	113·6	76	5	*11065*	*10988*	
18	,,	108·0	72	4	*11065*	*10992*	
19*a*	,,	53·9	100	6	*11095*	*10993*	
19*b*	,,	54·2	45	,,	*11016*	*10970*	
20	,,	108·1	72	,,	*11055*	*10982*	
21	24·6	263·6	169	5	7496	7470	
22	,,	213·6	136	,,	7507	7486	

TABLE II—(*contd.*)

No.	Temp. °C.	$p_1 - p_2$ mm.	p mean	No. of readings.	E−1	E−$1_{p=0}$	Remarks
			Nitrogenous fluorine compound of carbon $(CF_3N)_2$.				
1	27·6	599·6	405	5	3203	3145	
2	27·7	597·9	404	,,	3203	3145	
3	*−32·9*	370·7	249	7	*3365*	*3288*	Refractionated.
4*a*	,,	183·0	345	5	*3368*	*3263*	
4*b*	,,	188·2	158	6	*3316*	*3267*	
5	,,	371·2	250	5	*3344*	*3267*	
6	,,	372·5	,,	,,	*3347*	*3270*	
7	28·7	416·5	274	,,	3182	3143	
8*a*	,,	206·4	380	,,	3187	3133	
8*b*	,,	209·7	170	,,	3167	3143	
9	,,	416·1	273	,,	3178	3139	
10	*95·2*	453·5	293	6	*3052*	*3038*	
11*a*	,,	227·3	407	5	*3065*	*3045*	
11*b*	,,	225·9	179	,,	*3054*	*3045*	
12	,,	453·2	292	,,	*3061*	*3047*	
13	,,	453·1	,,	,,	*3056*	*3042*	
			Boron Hydride (B_2H_6).				
1	23·9	535·5	355	5	1785	1770	
2*a*	,,	267·3	491	,,	1791	1770	
2*b*	,,	268·1	221	,,	1782	1773	
3	,,	535·4	355	,,	1787	1772	
4	24·0	535·7	,,	,,	1785	1770	

TABLE II—(*contd.*)

No.	Temp. °C.	$p_1 - p_2$ mm.	p mean	No. of readings.	E−1	$E-1_{p=0}$	Remarks
			Boron Hydride (B_2H_6).—(contd.)				
5	*−79·8*	431·8	299	6	*1819*	*1776*	
6*a*	,,	213·3	409	,,	*1833*	*1774*	
6*b*	,,	218·4	192	,,	*1808*	*1780*	
7	,,	431·7	299	,,	*1820*	*1777*	
8	,,	431·8	,,	5	*1816*	*1773*	
9	24·4	530·6	351	,,	1799	1784	Trace of incondensible fraction removed.
10	,,	530·3	,,	,,	1797	1782	
11*a*	*95·2*	573·6	374	,,	*1756*	*1751*	Decomposing.
11*b*	*95·4*	575·7	375	,,	*1757*	*1752*	
11*c*	,,	577·3	376	,,	*1764*	*1759*	
			Nitrogenous boron hydride (tentative).				
1	24·1	25·4	16	6	2970	2920	
2	,,	,,	,,	5	2964	2914	
3	*95·2*	31·7	20	6	*2689*	*2671*	
4	,,	32·0	,,	4	*2733*	*2714*	
5	,,	32·2	,,	5	*2726*	*2707*	
6	25·2	21·3	13	,,	2998	2957	A little incondensible fraction removed next day.
7	,,	,,	,,	,,	3027	2986	

In Table III, the actual values of the compressibility corrections adopted in the calculations of $E-1_{p=0}$ are given as percentage corrections for a mean pressure of 380 mm. or for a change of pressure from 0 to 1 atmosphere.

TABLE III.

Percentage compressibility corrections.

	−80°	−33°	+25°	+95°
CF_4 ..	1·7	—	0·66	0·22
CHF_3 ..	3·5	—	0·77	0·26
NF_3 ..	2·0	—	0·66	0·22
$(CF_3N)_2$ ..	—	3·5	1·70	0·60
B_2H_6 ..	3·0	—	0·90	0·30
$B_3N_3H_6$ ..	—	—	40·0	13·0

The values at 25° have been obtained directly from refractometric measurements. Those at −33° and −80° have been calculated either from the study of the change of dielectric coefficient with pressure or have been estimated from corresponding values of other gases. The values at 95°, being usually very small, have been assumed to be approximately one-third of that at the ordinary temperature.

Before giving the actual values of polarisations and moments, it is desirable to give a brief account regarding individual measurements.

The values of *carbon tetrafluoride* at −80° and the later values at 25° agree. The slightly higher values at the steam temperature are not very significant and are within the limits of experimental error. The gas can therefore be regarded as having no electric moment.

Nitrogen trifluoride gave very steady and consistent values at all the temperatures at which the measurements were made. Repeated fractionations during the course of the series of experiments did not indicate any change in the values of dielectric coefficients. It may be mentioned that the present values are appreciably lower than those reported in an earlier paper.[4] It is intended to measure the density of the gas accurately and recompare the results.

Measurements on *fluoroform* could not be carried out at higher pressures owing to its high dielectric constant. The results however are sufficiently concordant to give an accurate measure of the electric moment.

[4] H. E. Watson, G. P. Kane and K. L. Ramaswamy, "Dielectric Coefficients of Gases", Part IV (Paper under publication).

The *nitrogen-carbon-fluorine* compound $(CF_3N)_2$ gave consistent values and has a measurable moment.

The initial values at the room temperature for *diborane* were a little lower than those measured later and this is probably due to a slow decomposition of the gas and further fractionation done. The values at the low temperature were steady and concordant and agreed with the values at the room temperature thus indicating a zero moment for the gas. At steam temperature the readings were rather unsteady and showed signs of decomposition and the results at this temperature, therefore, are not reliable.

Measurements with *nitrogenous boron hydride* $B_3N_3H_6$ were done at rather low pressures. Too much reliance cannot be placed on the values at the steam temperature since the vapour indicated a tendency to decompose. When the readings at the steam temperature were finished, the vapour was allowed to remain in the apparatus overnight, when it was found that the vapour which originally condensed very readily at solid carbon dioxide temperature contained a considerable amount of an incondensible fraction, probably hydrogen. If it be assumed that hydrogen is evolved as a result of heating to 95° C., the low values at the higher temperature are to be expected. Otherwise the existence of a moment for the gas is indicated.

In Table IV are given the mean values of $E-1_{\rho=0}$ and the values of molar polarisations calculated from the equation $P=\frac{E-1}{E+2}\cdot\frac{M}{D}$, at the

TABLE IV.

Mean values of $E-1_{\rho=0}$ *and polarisations.*

	−80° C.		−33° C.		25° C.		95° C.	
	E−1	P	E−1	P	E−1	P	E−1	P
CF_4 ..	1193	9·73	—	—	1192	9·72	1196	9·75
CHF_3 ..	10989	89·28	—	—	7484	60·88	6272	51·04
NF_3 ..	1287	10·50	—	—	1220	9·95	1203	9·81
$(CF_3N)_2$ ..	—	—	3269	26·63	3142	25·60	3043	24·79
B_2H_6 ..	1776	14·47	—	—	1774	14·46	1755	14·30*
$B_3N_3H_6$ ..	—	—	—	—	2917	23·76	2697	21·97*

* Not reliable.

temperatures mentioned. Since the figures for $E-1_{\rho=0}$ represent the values corrected for deviations from Boyle's law and $\frac{M}{D}$ is the molecular volume and $E+2$ for most gases is not far from 3, the polarisations are obtained by multiplying $E-1_{\rho=0}$ by the factor ·008155. Wherever E becomes quite appreciable, the necessary correction in $E+2$ has been made.

In the case of fluoroform for which the different values at the room temperature have been carried out at slightly varying temperatures, the polarisation at 25° has been obtained by interpolation.

Electric Moments.

The values of A and B in Debye's equation $P=A+B/T$ calculated from the data in Table IV, and of the electric moment μ obtained from the expression $B=4\pi N\mu^2/9k$ are given in Table V. Substituting the values of Avogadro's number, $6\cdot06\times10^{23}$, and Boltzmann's constant k, $1\cdot372\times10^{-16}$, the expression becomes $\mu\times10^{18}=0\cdot01272\sqrt{B}$.

TABLE V.

Values of A, B and μ.

	Temp. range in °C. (Absolute)	A	B	$\mu\times10^{18}$
NF_3 ..	298—368	9·22	219	0·19
	298—193	8·94	303	0·22
	Mean	9·08	261	0·21
CHF_3 ..	298—368	9·23	15400	1·58
	298—193	8·48	15630	1·59
	Mean	8·86	15515	1·59
$(CF_3N)_2$ ..	301—368	21·16	1337	0·47
	301—240	21·54	1223	0·44
	Mean	21·35	1280	0·46
$B_3N_3H_6$ ..	298—368	(14·36)	(2802)	(0·67)†

† Tentative.

The small differences in the values of moments between two ranges of temperature are probably due to slight errors in the measured or assumed values of compressibilities and cannot therefore be taken as proving the

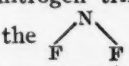
inapplicability of the Debye's equation. The mean values have been taken as the most probable in discussing the structures of these molecules.

Discussion.

Nitrogen trifluoride.—The small moment observed for this gas can be explained on the basis of the electronegativity scale as given by Malone and Ferguson.[5] According to these authors, taking hydrogen as standard (H=0), the values given for N and F are 1·04 and 1·72. These values indicate that the moment of nitrogen trifluoride will be far less than that of ammonia. This view is in agreement with the high value of the moment of 1·49 observed by Watson[6] for ammonia.

On comparing the analogous compounds of arsenic (electronegativity=0·10)[5], arsenic trifluoride should have a larger value for the electric moment than arsine. Actually, the observed moment for arsine[6] and arsenic trifluoride[5] are 0·15 and 2·65 respectively.

From these considerations, one can say that the value of the moment for nitrogen trichloride should be nearly zero, since the electronegativity of chlorine[5] atom is not appreciably different from that of nitrogen, the values being 1·03 and 1·04 respectively. No measurements have so far been made to verify this result.

On account of the high electronegative value for fluorine, the three fluorine atoms in nitrogen trifluoride will repel each other considerably, increasing thereby the  valency angle to nearly 120°. The exact value of N—F link moment being undetermined, the actual valency angle in nitrogen trifluoride cannot be calculated at present.

Fluoroform.—The observed moment of fluoroform is appreciably larger than that for chloroform (μ=0·95), measured by Sänger[7] in the gaseous state.

As has been assumed with chlorobenzene, the moment of fluorobenzene (μ=1·43) also, can be regarded as giving an estimate of C—F bond moment. This value agrees with C—F moment calculated from the value of the moment 1·81 for methyl fluoride[8], assuming as usual that C—H moment is 0·4. Substituting the value of C—H moment in the observed value for fluoroform, the moment of CF_3 group comes out as 1·6−0·4=1·2. If the C—F moment

[5] M. G. Malone and A. L. Ferguson, *Jour. Chem. Phys.*, 1934, **2**, 99.

[6] H. E. Watson, *Proc. Roy. Soc.*, A, 1927, **117**, 43.

[7] R. Sänger, *Physik. Z.*, 1926, **27**, 556.

[8] C. P. Smyth and K. B. McAlpine, *J. Chem. Physics*, **1**, 190.

were 1·4 and the tetrahedral angle prevailed in CF_3 radicle, the group moment should be 1·4. The smaller value of CF_3 group estimated from actual observed moment for fluoroform, would indicate, therefore, that the valency angles are more than tetrahedral. A similar spreading of valencies has already been observed in the case of chloroform by Bewilogua.[9]

New compound of carbon, nitrogen and fluorine ($CF_3N)_2$.—Prof. Dr. Otto Ruff in a private communication, suggests four alternative structures for this compound as represented below :

(1) $F_3C-N=N-CF_3$

(2) $F_3C-N=CF-NF_2$

(3) F_2C-NF / $FN-CF_2$

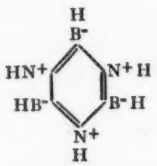
(4) F_2C-NF / F_2C-NF

Of these (1) and (2) can exhibit *cis* and *trans* isomerism since the angle between a single bond and a double bond is usually 125°. Thus six structures are possible for this compound.

Of these six structures, tranform of (1) and form (3) will have zero moment. The calculation of moments for structures (2) and (4) are difficult since the link moments of N=C and N−F are not known with certainty but they indicate the possibility of the existence of a high moment. Approximate calculations however indicate that the *cis* form of (1) would give a moment of the order observed ; the simplicity of this structure would also support such an assignment.

For a definite understanding of the structure further physical data are necessary. It is intended to do the Raman effect which may throw some light on the subject.

Nitrogenous boron hydride ($B_3N_3H_6$).—Stock[3] and co-workers from considerations of stability, addition reactions and other physical data such as density, electron diffraction,[3] have come to the conclusion that the most probable structure for the compound is that of a plane hexagon with alternate boron and nitrogen atoms, the six hydrogen atoms being attached to the six atoms as in benzene. It is shown diagrammatically in the figure.



On account of the uncertainty in the values at the steam temperature, the significance of the observed moment cannot be emphasised. If the moment is assumed to be correct, it cannot be explained by such a plane symmetrical structure.

[9] Bewilogua, *Physik. Z.*, 1931, **32**, 265.

The refractive index and the dispersion have been done for the vapour and the results will be given in a separate paper. The calculated refractivity for infinite wave-length comes to 20·1. Adding fifteen to twenty per cent. (the contribution of atom polarisation for fluorine and boron compounds as will be explained in a later paper) to the electron polarisation, the displacement polarisation is almost equal to the total polarisation thus indicating a zero moment for the compound.

In view of these facts the results are given as tentative and require further confirmation.

Boron hydride.—The absence of an electric moment for the diborane can only indicate that the molecule has a symmetrical structure with possibly a co-valent linkage between the two boron atoms. The question of exact configuration cannot be settled without other experimental data.

Summary.

1. The dielectric coefficients of CF_4, NF_3, CHF_3, $(CF_3N)_2$, B_2H_6 and $B_3N_3H_6$ (in the vapour state) have been measured at different temperatures to obtain the values of their electric moments. These values are 0, 0·21, 1·59, 0·46, 0 and $0 \cdot 67 \times 10^{-18}$ respectively.

2. Accurate measurements of compressibilities at the ordinary temperature by refractometric studies and approximate values at low temperatures by studying variations of dielectric coefficients, have been made.

3. The significance of the moments has been briefly discussed.

In conclusion I wish to express my deep indebtedness to Prof. Dr. Otto Ruff, Breslau, for the gift of the fluorine compounds and to Prof. Dr. Alfred Stock, Karlsruhe, for the gift of the boron compounds. My grateful thanks are due to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his kind encouragement and keen interest in the work.

My thanks are also due to Dr. M. A. Govinda Rau for his help in the discussion of the structure of some of the compounds.

THE PHYSICAL IDENTITY OF ENANTIOMERS.

Part I.[1] Rotatory Dispersion of *Lævo*-Borneol, Enantiomeric Camphors, Camphoric Acids, Sodium Camphorates, Camphoric Anhydrides and Camphorimides.

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According to Pasteur's principle of molecular dissymmetry, enantiomorphous molecular configurations must possess the same total energy. They must show similar mechanical stability, and, therefore, have an equal chance of being produced. They must also possess the same scalar properties, such as density, viscosity, crystal lustre, solubility, refraction, dispersion and Raman frequencies. But they must differ in those physical properties, which are of the directional (vectorial) nature, such as, for example, direction of rotation of the plane of polarisation of polarised light, unsymmetrical distribution of the hemihedral facets in their crystal forms, and also in the enantiomorphous distribution of pyro- and piezo-electrical polarity. The magnitude of these vectorial properties is, however, identical for the enantiomorphous forms. These results follow from classical mechanics. On the other hand, according to wave-mechanics,[2] the *dextro-* and *lævo*-forms of a compound differ in energy and in rotatory power, although perhaps only to a very slight extent. The two views thus lead to different results. In support of the view derived from wave-mechanics, slight but distinct differences are alleged to exist in the rotatory power and other physical properties of the *dextro-* and *lævo*-forms of mandelic and camphoric acids.[3] But Pasteur's Law of Molecular Dissymmetry is too fundamental to be dismissed by a few isolated observations; the discrepancies in these cases may very well be due to some impurities in the substances examined. It seems impossible that the *d*- and *l*-forms of a compound could be other than an object

[1] For a preliminary note on this subject, see B. K. Singh, *Current Science*, 1935, **3**, 420–421.

[2] G. Temple, *Trans. Faraday Soc.*, 1930, **26**, 272.

[3] A. N. Campbell and F. C. Garrow, *Trans. Faraday Soc.*, 1930, **26**, 560; A. N. Campbell, *J. Amer. Chem. Soc.*, 1931, **53**, 1661.

and its non-superposable exact mirror-image, agreeing precisely in every detail of structure and of properties, except those of a vectorial nature, which differ in sign, but are otherwise identical in the ***numerical magnitude*** in all cases. Moreover, it must be borne in mind that the wave-mechanics of rotatory polarisation is, at present, in a rather unsatisfactory condition.

With this object of testing the validity of Pasteur's Law as regards the equality in the numerical values of the rotatory power of the opposite and active forms, an extended series of investigations on the rotatory dispersion of enantiomorphous forms was undertaken in this laboratory. Out of 1800 observations on the rotatory power which have been recorded[4] and those which still await publication, the differences in the specific rotatory power of the *dextro-* and *lævo*-forms correspond to a difference which is within 0·01° in the observed angle of rotation in 80 percent. cases, between 0·01° and 0·02° in 17 percent. cases, between 0·02° and 0·03° in 2·5 percent. cases, and between 0·03° and 0·04° in the remaining one half percent. cases, the maximum deviation allowable in such observations being 0·02° in the observed angle of rotation. The three percent. cases, in which the differences are slightly greater than the maximum allowable deviation (0·02°) for certain wave-length, give values for rotatory power for other wave-lengths, which are within the maximum error. This shows that these deviations are of the nature of casual experimental errors.

The recent observations of Darmois[5] on the rotatory power of the *d*- and *l*-forms of the complex ammonium salts of molybdic and malic acids of the formula $[4\,MoO_3,\ 2C_4H_4O_5]\ (NH_4)_4+5H_2O$ for mercury green light, show that the observed angles of rotation do not differ by more than 1 part in 1,000 parts.

These results clearly support Pasteur's principle of molecular dissymmetry, according to which the *d*- and *l*-forms are represented as true mirror-images of one another, differing in sign, but absolutely identical in the numerical value of the rotatory power.

The two cases of mandelic and camphoric acids in which discrepancies in the equality of the numerical values of the rotatory power have been noticed by Campbell and Garrow,[6] however, militate against Pasteur's principle. It is, therefore, of very great importance to re-examine these

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[4] B. K. Singh and B. Bhaduri, *J. Indian Chem. Soc.*, 1930, **7**, 54, 771; 1931, **8**, 181, 623; *Trans. Faraday Soc.*, 1930, **26**, 347; B. K. Singh, H. P. Basu-Mallik and B. Bhaduri, *J. Indian Chem. Soc.*, 1931, **8**, 95; B. K. Singh, B. Bhaduri and T. P. Barat, *ibid.*, 1931, **8**, 345.

[5] Darmois, *Bull. Soc. Fr. Physique*, 1931, **301**, 23.

[6] Campbell and Garrow, *loc. cit.*

cases with a view to ascertain how far they can be substantiated. In the case of mandelic acid, Körtum[7] finds that if the preparations are sufficiently purified, measurable differences in the specific rotation of *d*- and *l*-mandelic acids are not observed. Campbell[8] has replied to this work of Körtum,[9] but it is unconvincing and ineffective. Moreover, there is no further experimental data and the reply is only of a polemic nature. We have now determined the rotatory powers of *d*- and *l*-camphoric acids in acetone, ethyl alcohol, and water for 10 different wave-lengths (λ=4358 to 6709 Å). The *d*-camphoric acid was prepared from *d*-camphor and *l*-camphoric acid from *l*-borneol as detailed in the experimental part. Campbell's method[10] of preparation of these acids was followed so as to leave no room for doubt for any discrepancy. Taking the maximum deviation allowable in such polarimetric observations of 0·02° in the observed angle of rotation for 5 percent. acetone and ethyl alcoholic solutions of camphoric acid (Tables IV and VII), the specific rotation of the *dextro*- and *lævo*-camphors can differ by about 0·2°. Actually we find that in the case of camphoric acid in acetone solution, the specific rotation of the *d*-form is greater than that of the *l*-form by 0·7° for λ=4358 and is less by 0·6° for λ=6709. For other 8 wave-lengths the differences in the specific rotation are less than 0·2°. In ethyl alcohol (Table VII), the specific rotation of *d*-form is less than that of *l*-form by 0·4° for λ=4358 and greater by 0·3° for λ=5086. For other 8 wave-lengths the differences are within the experimental error. Similarly in aqueous solution, the difference in the rotatory power of *d*- and *l*-forms of camphoric acid (Table X) and of sodium camphorate (Table XI) are within the experimental error for all the 10 wave-lengths.

The effect of concentration on the rotatory dispersions of *d*- and *l*-camphoric acids in ethyl alcohol for 10 $\lambda\lambda$ between 4358 and 6709 Å has also been studied : it is found that the rotatory power at first decreases with increase in concentration and then becomes almost constant (*vide* Table A and Fig. 1). These values further establish the identity of the magnitude of the rotatory power of the two opposite and active forms.

Incidentally the rotatory dispersions of *l*-borneol (Tables XIV and XV), *d*- and *l*-camphor (Tables I, II and III) and *d*- and *l*-camphorimide (Tables XVI, XVII and XVIII) have also been determined and found to be identical within the limits of experimental error. Pasteur's law of molecular dissymmetry is thus shown to hold good also in the case of these substances,

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[7] Körtum, *Ber.*, 1931, **64B**, 1506.
[8] Campbell, *Ber.*, 1931, **64B**, 2476.
[9] Körtum, *loc. cit.*
[10] Campbell, *Jour. Amer. Chem. Soc.*, 1931, **53**, 1662.

TABLE A.

Specific Rotation of d- *and* l-*Camphoric Acids in Ethyl Alcohol at* 35° C. *at different concentrations.*

(length of tube, 2 dcm.)

Line	Form	*dextro*	*lævo*	*dextro*	*lævo*	*dextro*	*lævo*	*dextro*	*lævo*	*dextro*	*lævo*
	Concentration g/100 c.c.	1·2533	1·2526	3·2467	3·2473	5·2530	5·2500	7·2500	7·2507	9·2500	9·2480
Hg_{4358}		+98·94°	−97·40°	+96·15°	−95·62°	+94·41°	−94·87°	+94·37°	−94·76°	+93·30°	..
Cd_{5086}		70·61	70·70	66·66	66·99	66·24	65·92	66·00	65·93	65·21	−65·23°
Ag_{5209}		65·83	66·26	63·46	63·33	62·63	62·86	62·40	62·50	62·03	61·99
Hg_{5461}		59·44	59·08	56·84	56·83	56·35	56·19	56·21	56·12	55·40	55·46
Ag_{5469}		59·04	59·08	56·84	56·82	56·15	56·19	55·86	55·78	55·49	55·41
Hg_{5750}		51·46	51·89	49·90	49·89	49·68	49·71	49·38	49·38	48·91	49·08
Na_{5892}		49·87	50·30	48·07	48·20	47·79	47·80	47·44	47·38	46·95	47·02
Li_{6104}		45·47	44·71	44·51	44·66	43·97	44·15	43·79	43·65	43·71	43·78
Cd_{6438}		41·09	41·52	39·67	39·42	39·41	39·44	39·03	39·24	39·06	38·97
Li_{6709}		37·50	36·32	36·22	36·19	35·98	35·82	35·72	35·66	35·62	35·56

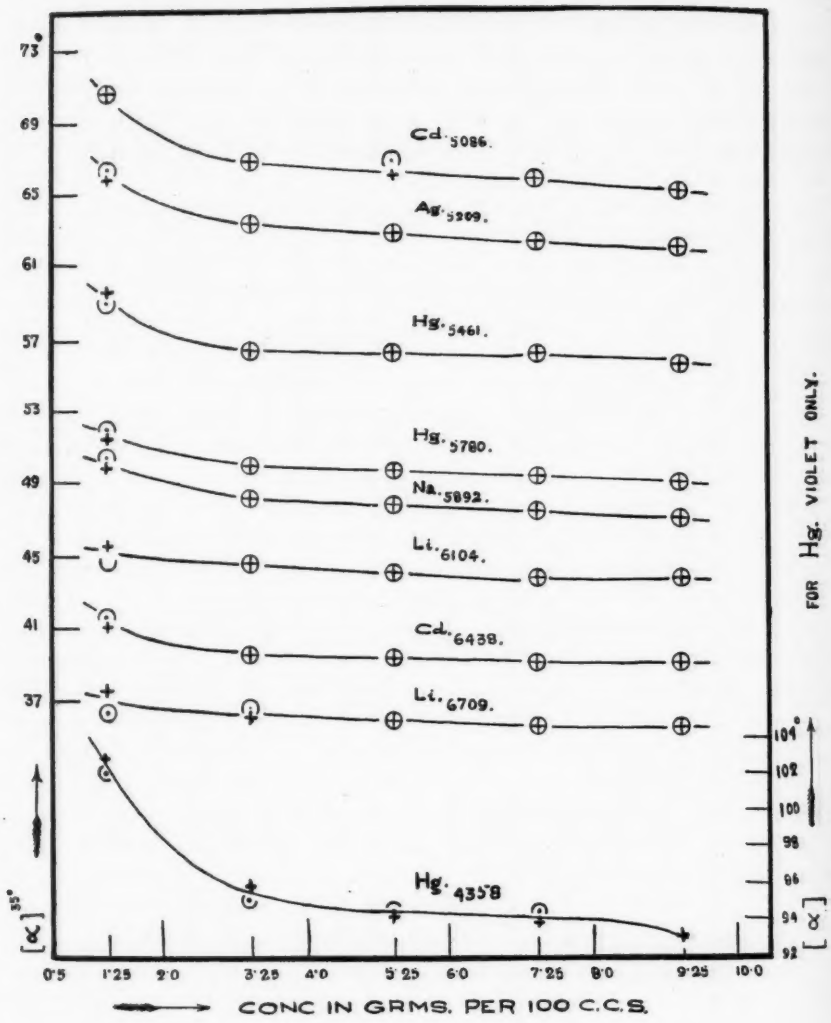

FIG. 1.

Rotatory dispersion of *d*- and *l*-camphoric acids at different concentrations in ethyl alcohol at 35°C.

⊕ indicates *dextro*

⊙ „ *lævo*

⊕ „ identical values of *dextro* and *lævo*

viz., mandelic acids and camphoric acids, in which discrepancies were previously noticed. They possess identical rotatory power if sufficient care is taken to purify the substances. The rotatory powers of *d*-camphor and *l*-borneol have been determined by Lowry[11] at 20°, but we find higher values for these compounds at 35° (Tables II and XIV) : *viz.*—for λ_{5461} the value of $[\alpha]$ for *l*-borneol is 45·21° for 6·9 percent. solution (in benzene) against 32·55° of Lowry for 22·5 percent. solution (in benzene) at 20° and for *d*-camphor $[\alpha]=59·79°$ for 33 percent. solution (in benzene) at 35° against $[\alpha]=56·72°$ of Lowry, for the same concentration at 20°. For other lines the tables of rotatory dispersions (Tables II and XIV) may be consulted. It seems, therefore, that Lowry's materials may be slightly impure as the temperature coefficient of rotatory power is unlikely to be so high.

Types of Rotatory Dispersion.

Camphoric acid, sodium camphorate, and camphorimide follow Drude's Law of Simple Dispersion $[\alpha]=\frac{k}{\lambda^2-\lambda_0^2}$, whereas *l*-borneol and camphor exhibit complex rotatory dispersion and follow the two-term equation,

$$[\alpha] = \frac{k_1}{\lambda^2-\lambda_1^2} \pm \frac{k_2}{\lambda^2-\lambda_2^2}$$

Relation between Chemical Constitution and Rotatory Power.

(*a*) *The Effect of Cyclic Structure on Rotatory Power.*—The rotatory power of a cyclic compound is usually considerably different from that of the corresponding open-chain derivative. This is evident from the following instances, which show that when an open-chain, optically active compound is transformed into a ring compound, this is always accompanied by a marked change in rotatory power—in some cases there is a marked increase, while in others there is a considerable decrease in the value of this property. Thus the rotatory powers of esters of 1-methyl-3-cyclopentanone-4-carboxylic acid are about thirty times as great as those of the corresponding esters of methyl-adipic acid,[12] and the hexahydrophthalic acids have much lower rotatory powers than their anhydrides.[13] This rule is more strikingly borne out in the case of derivatives of monosaccharides. The rotatory power of *d*-mannitol[14] is $[\alpha]_D^{20°} = -0·2°$, whereas that of *d*-mannonolactone[15] is $-53·8°$. The high rotatory power of most of the sugars as compared with the corresponding polyhydric alcohols is a proof of the ring structure of

[11] Lowry and Cutter, *J.C.S.*, 1925, **127**, 614.

[12] Haller, *Compt. Rend.*, 1905, **140**, 1205.

[13] Werner, *Ber.*, 1899, **32**, 3046.

[14] Fischer, *Ber.*, 1890, **23**, 3684.

[15] Fischer, *Ber.*, 1889, **22**, 3219.

the former. The increase which is brought about in the rotatory power of sugar alcohols by boric acid is attributed to the formation of ring complexes. Instances in which ring formation leads to a phenomenal depression in optical activity are to be found in derivatives of camphor. The camphoric acids and their anhydrides afford good illustrations of this rule, the acids having $[\alpha]^{35°}_{Hg_{5461}} = 56 \cdot 35°$ in ethyl alcohol (Table VII), whilst the anhydrides are optically inactive throughout the whole range of spectrum investigated from $\lambda = 4258$ to 6709 (Table XII). That this is not due to racemisation follows from the fact that both the *dextro-* and *lævo-*camphoric anhydrides ($[\alpha] = 0 \cdot 0°$) on hydrolysis yield the optically active acids of correct rotatory power (*see* p. 386). Camphoramic acids and their anhydride provide another illustration, the acids having $[\alpha]_D = 45°$ (α), 60° (β) in ethyl alcohol, while the anhydride has $[\alpha]_D = 9 \cdot 15°$ (Table XVI). Other similar cases of marked differences in rotatory power of the aryl derivatives of *d*-camphorimide and *d*-camphoramic acid have already been pointed out by one of us[16] in previous communications.

(*b*) *The Effect of Substitution in the Ketomethylene Group of Camphor on its Rotatory Power.*—On comparing the structural formulæ of these compounds with their rotatory power (Table B), the following conclusions may be drawn.

The reduction of the keto group in camphor ($[\alpha]^{35°}_{Hg_{5461}} = 59 \cdot 61°$) to the carbinol group in borneol ($[\alpha]^{35°}_{Hg_{5461}} = 43 \cdot 45°$) is accompanied by only a small depression in rotatory power, whereas the conversion of the ketomethylene group to diketo group in camphorquinone ($[\alpha]^{35°}_{Hg_{5461}} = 165 \cdot 5°$) is accompanied by a very great rise in rotatory power and that to the ketoxime group in isonitrosocamphor ($[\alpha]^{35°}_{Hg_{5461}} = 241 \cdot 2°$) is attended with a still greater rise in rotatory power. The oxidation of the ketomethylene group to two carboxyl groups as in camphoric acid ($[\alpha]^{35°}_{Hg_{5461}} = 56 \cdot 35°$) has hardly any effect on rotatory power. The ring formation in camphoric acid by an oxygen atom as in camphoric anhydride ($[\alpha]^{35°}_{Hg_{5461}} = 0 \cdot 0°$) leads to a phenomenal depression in rotatory power, whereas that by an imido group as in camphorimide ($[\alpha]^{35°}_{Hg_{5461}} = 11 \cdot 25°$), though still accompanied by considerable depression, does not produce this effect to the same extent.

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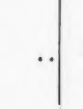
[16] B. K. Singh and A. C. Biswas, *J. Chem. Soc.*, 1924, **125**, 1895; B. K. Singh and A. N. Puri, 1926, 504.

TABLE B.

Name	Formula	$[\alpha]^{35°}_{Hg_{5461}}$ (Ethyl Alcohol)
d- and *l*- Camphor		± 59·61°
„ Borneol		± 43·45°
„ Isonitrosocamphor (stable)		± 241·20
„ Isonitrosocamphor (unstable)		± 214·28
„ Camphorquinone		± 165·54
„ Camqhoric acid		± 56·35
„ Camphorimide		± 11·26
„ Camphoric Anhydride ..		± 0·00

Experimental.

l-*Borneol.*—*l*-Borneol employed in this work had the following constants : m.p. 203–204° C. ; $[\alpha]^{35°}_{Hg_{5461}}$, −43·45° and $[\alpha]^{35°}_{Na_{5893}}$, −36·42° for 11·6 percent. solution in ethyl alcohol ; whereas Lowry's values are as follows : m.p. 204° C. ; $[\alpha]^{20°}_{Hg_{5461}}$, −43·27° and $[\alpha]^{20°}_{Na_{5893}}$, −37·30° for 7·7 percent. olution in ethyl alcohol.

l-*Camphor.*—*l*-Camphor was prepared from *l*-borneol and had a m.p. 178° C. and the following rotatory dispersion values : $[\alpha]^{35°}_{Hg_{5461}}$, −59·48° and $[\alpha]^{35°}_{Na_{5893}}$, −46·44° for 33 percent. solution in ethyl alcohol. Also purified *d*-camphor gave nearly identical m.p. and rotational values, *viz.*, $[\alpha]^{35°}_{Hg_{5461}} = 59·6°$ and $[\alpha]^{35°}_{Na_{5893}} = 46·53°$ for the same concentration and solvent.

d-*Camphoric Acid and* d-*Camphoric Anhydride.*—*d*-Camphoric acid was prepared by the method of Campbell[17] from camphor having the above constants. *d*-Camphor (48 g.) was introduced into a round-bottomed flask with a ground-on air condenser, to which a mixture of concentrated nitric acid (384 c.c.) of d. 1·42 and water (256 c.c.) were added and refluxed for about 60 hours on a water-bath with occasional shaking, at the end of which crystals began to appear on cooling. The crystals were filtered off. The yield was 34 g. The crude acid was then dissolved in about 120 c.c. of 10 percent. caustic soda solution and shaken twice with ether to remove any unchanged camphor after which it was reprecipitated with HCl (1 : 1) till acid and filtered. Yield : 25 g. ; m.p. 182–184° C. The purified acid was next treated with excess of acetyl chloride (50 g.) and refluxed for one hour. On shaking with cold water, the excess of acetyl chloride was removed. The anhydride was then crystallised from boiling ethyl alcohol and it melted at 221° C. The anhydride was hydrolysed by boiling with potassium carbonate solution. The acid was precipitated by neutralising the alkaline solution with hydrochloric acid. The precipitate was filtered, washed and crystallised four times from boiling water, taking care to reject the first crop. Yield : 7 g. (in cubes) ; m.p. 187° C.

l-*Camphoric Acid and* l-*Camphoric Anhydride.*—*l*-Camphoric acid was prepared by the oxidation of *l*-borneol with nitric acid. *l*-Borneol (50 g.) and a mixture of 384 c.c. nitric acid (d. 1·42) and 256 c.c. water were taken in a flask with a ground-on air condenser and refluxed on a boiling water-bath for about 60 hours. The crystals were filtered off and dissolved in 10 percent. caustic soda solution and shaken with ether to remove unchanged borneol and camphor. The alkaline solution on being neutralised with hydrochloric acid gave a precipitate of *l*-camphoric acid which was then treated with excess of acetyl chloride and refluxed for one hour. The excess of acetyl chloride was removed by mixing this with cold water. The *l*-camphoric anhydride was filtered off and crystallised from boiling ethyl alcohol. Yield : 23 g. ; m.p. 221° C. On boiling with potassium carbonate solution and neutralising the alkaline solution with hydrochloric acid, *l*-camphoric acid was precipitated and crystallised four or five times from boiling water, the first crop being rejected each time. Yield : 6 g. ; m.p. 187° C.

dl-*Camphoric Acid and* dl-*Camphoric Anhydride.*—These were also prepared in the same way as the *dextro*-isomeride from purified *dl*-camphor.

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[17] Campbell, *J. Amer. Chem. Soc.*, 1931, **50**, 1662.

dl-Camphoric acid melted at 202–203° C. and *dl*-camphoric anhydride at 221° C.

It should be noted that although *dl*-camphoric acid differed in melting point from that of either of the active isomerides, *dl*-camphoric anhydride had the same melting point as that of its *dextro*- or *lævo*-isomeride. *d*- and *l*-Camphoric anhydrides are optically inactive for the whole range of spectrum investigated (λ=4258 to 6709 Å) (Tables XII and XIII), but yield, on hydrolysis, the corresponding optically active acids with $[\alpha]_D = +47{\cdot}79°$ and $-47{\cdot}80°$ respectively.

Sodium Salts of Camphoric Acid.—These salts were prepared by neutralising the corresponding acids with sodium bicarbonate solution and crystallising from aqueous solution. They crystallise with 5 molecules of water of crystallisation. 0·154 g. of salt gave on dehydration 0·567 g. of the anhydrous salt. Found, 89·85 g. of water per molecule; Calculated, 90·0 g. of water per molecule. 0·154 g. of salt gave 0·0654 g. of Na_2SO_4. Found, 141·84 g. of Na_2SO_4 per molecule; Calculated, 142 g. of Na_2SO_4 per molecule.

d-*Camphorimide.*—20 g. of *d*-Camphoric acid are introduced into an iron retort with a long wide glass tube as condenser and an inlet tube reaching almost to the bottom of the retort. The retort is heated in a lead bath and a slow current of ammonia gas, dried by passing through lime and sodalime towers, is led into the fused mass. The current is made rapid as the mass boils and a white partially gummy substance distils over into the condenser. After scraping it off, it is again returned to the retort and distilled in a more rapid current of ammonia as before. The solid distillate which is now deposited in the glass condenser, is a white mass of needle-like crystals. Yield: 4 g. It is then crystallised from alcohol as colourless needle-shaped prisms melting at 242–243° C.

l-*Camphorimide.*—This was prepared in the same way as the corresponding *dextro*-isomer and has the same melting point, solubility and rotatory power (Tables XVI, XVII and XVIII). (Found: C, 66·24; H, 8·50; N, 8·2. $C_{10}H_{15}O_2N$ requires C, 66·66; H, 8·33; N, 8·4 percent.)

dl-*Camphorimide.*—It was prepared in the same way as its optically active isomers and melts at 242–243° C. (Found: N, 8·3; $C_{10}H_{15}O_2N$ requires N, 8·4 percent.).

The rotatory power determinations were made in a 2-dcm. tube (jacketed) at 35°C. except in the cases of *d*- and *l*-camphor in benzene and ethyl alcohol where a 1-dcm. tube was employed. The value of λ_0, calculated from the dispersion formula, is given in the tables and is expressed as μ or 10^{-4} cm.

TABLE I. *Camphor in Acetone.*

$$[\alpha] = \frac{18{\cdot}4}{\lambda^2 - 0{\cdot}0922} - \frac{6{\cdot}95}{\lambda^2}$$

Dextro			Line λ	Calc. $[\alpha] = c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha] = o$	$o - c$			$o' - c$	Obs. $[\alpha] = o'$	Concentration g/100 c.c.
29·82	+83·82°	+0·10°	Cd_{5086}	±83·72°	+0·16°	−83·88°	29·50
,,	77·10	−0·03	Ag_{5209}	77·13	−0·02	77·11	,,
,,	66·02	+0·03	Hg_{5461}	65·99	+0·03	66·02	,,
,,	55·26	−0·01	Hg_{5780}	55·27	−0·06	55·21	,,
,,	52·04	−0·13	Na_{5893}	52·17	−0·17	52·00	,,
,,	47·01	+0·04	Li_{6104}	46·97	+0·02	46·99	,,
,,	36·11	+0·15	Li_{6709}	35·96	+0·18	36·14	,,

No mutarotation.

TABLE II. *Camphor in Benzene.*

$$[\alpha] = \frac{29{\cdot}87}{\lambda^2 - 0{\cdot}0852} - \frac{19{\cdot}96}{\lambda^2 - 0{\cdot}0521}$$

Dextro			Line λ	Calc. $[\alpha] = c$	*Lævo*		
Concentration g/100 c..c.	Obs. $[\alpha] = o$	$o - c$			$o' - c$	Obs. $[\alpha] = o'$	Concentration g./100 c.c.
33·5400	+75·80°	+0·20°	Cd_{5086}	±75·60°	+0·25°	−75·85°	33·5035
,,	70·04	+0·62	Ag_{5209}	69·42	+0·43	69·85	,,
,,	59·70	−0·09	Hg_{5461}	59·79	−0·14	59·65	,,
,,	49·22	+0·02	Hg_{5780}	49·20	+0·11	49·31	,,
,,	46·38	±0·00	Na_{5893}	46·38	+0·03	46·41	,,
,,	41·63	−0·07	Li_{6104}	41·70	±0·00	41·70	,,
,,	35·46	−0·16	Cd_{6438}	35·62	−0·04	35·58	,,
,,	31·70	+0·02	Li_{6709}	31·68	+0·14	31·82	,,

No mutarotation.

TABLE III. *Camphor in Ethyl Alcohol.*

$$[\alpha] = \frac{11{\cdot}03}{\lambda^2 - 0{\cdot}1484} - \frac{0{\cdot}093}{\lambda^2 - 0{\cdot}2253}$$

Dextro			Line λ	Calc. $[\alpha]$ $= c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ $= o$	$o - c$			$o' - c$	Obs. $[\alpha]$ $= o'$	Concentration g./100 c.c.
33·5415	+75·98°	−0·20°	Cd_{5086}	±76·18°	−0·08°	−76·10°	33·5420
,,	70·10	+0·38	Ag_{5209}	69·72	+0·26	69·98	,,
,,	59·61	+0·24	Hg_{5461}	59·37	+0·12	59·49	,,
,,	49·87	+0·16	Hg_{5780}	49·71	+0·15	49·86	,,
,,	46·93	−0·04	Na_{5893}	46·97	−0·12	46·85	,,
,,	42·11	−0·27	Li_{6104}	42·38	−0·18	42·20	,,
,,	36·41	−0·11	Cd_{6408}	36·52	+0·08	36·60	,,
,,	32·52	−0·16	Li_{6708}	32·68	−0·08	32·60	,,

No mutarotation.

TABLE IV. *Camphoric Acid in Acetone.*

$$[\alpha] = \frac{15{\cdot}57}{\lambda^2 - 0{\cdot}0391}; \quad \lambda_o = 0{\cdot}1977$$

Dextro			Line λ	Calc. $[\alpha]$ $= c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ $= o$	$o - c$			$o' = c$	Obs. $[\alpha]$ $= o'$	Concentration g./100 c.c.
5·4680	+105·80°	+2·6°	Hg_{4358}	±103·2°	+1·8°	−105·10°	5·4760
,,	70·30	−0·61	Cd_{5086}	70·91	−0·71	70·20	,,
,,	67·54	+0·41	Ag_{5209}	67·13	+0·24	67·37	,,
,,	60·14	+0·06	Hg_{5461}	60·08	−0·02	60·06	,,
,,	59·78	−0·14	Ag_{5468}	59·92	+0·06	59·98	,,
,,	53·11	+0·33	Hg_{5780}	52·78	−0·44	53·22	,,
,,	50·46	−0·09	Na_{5893}	50·55	+0·11	50·66	,,
,,	47·34	−0·36	Li_{6104}	47·70	−0·41	47·29	,,
,,	41·76	+0·28	Cd_{6438}	41·48	+0·33	41·81	,,
,,	38·03	+0·13	Li_{6709}	37·90	+0·72	38·62	,,

No mutarotation.

TABLE V. *Camphoric Acid in Ethyl Alcohol.*

$$[\alpha] = \frac{14 \cdot 84}{\lambda^2 - 0 \cdot 0477}\ ;\ \lambda_0 = 0 \cdot 2184$$

Dextro			Line λ	Calc. $[\alpha]$ $= c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ $= o$	$o - c$			$o' - c$	Obs. $[\alpha]$ $= o'$	Concentration g./100 c.c.
1·2533	+103·50°	−0·80°	Hg_{4358}	±104·30°	−1·55°	−102·75°	1·2526
,,	70·61	+0·28	Cd_{5086}	70·33	+0·37	70·70	,,
,,	65·83	−0·55	Ag_{5209}	66·38	−0·12	66·26	,,
,,	59·44	+0·19	Hg_{5461}	59·25	−0·17	59·08	,,
,,	59·04	−0·01	Ag_{5468}	59·05	+0·03	59·08	,,
,,	51·46	−0·36	Hg_{5780}	51·82	+0·07	51·89	,,
,,	49·87	+0·30	Na_{5893}	49·57	+0·73	50·30	,,
,,	45·47	−0·21	Li_{6104}	45·68	−0·97	44·71	,,
,,	41·09	+0·63	Cd_{6438}	40·46	+1·06	41·52	,,
,,	37·50	+0·60	Li_{6709}	36·90	−0·58	36·32	,,

No mutarotation.

TABLE VI. *Camphoric Acid in Ethyl Alcohol.*

$$[\alpha] = \frac{15 \cdot 14}{\lambda^2 - 0 \cdot 0320}\ ;\ \lambda_0 = 0 \cdot 1788$$

Dextro			Line λ	Calc. $[\alpha]$ $= c$	*Lævo*		
Concentration g./100 c.c	Obs. $[\alpha]$ $= o$	$o - c$			$o' - c$	Obs. $[\alpha]$ $= o'$	Concentration g./100 c.c.
3·2467	+96·15°	+0·37°	Hg_{4358}	±95·78°	+0·16°	−95·62°	3·2473
,,	66·66	−0·10	Cd_{5086}	66·76	+0·23	66·99	,,
,,	63·46	+0·21	Ag_{5209}	63·25	+0·08	63·33	,,
,,	56·84	−0·03	Hg_{5461}	56·87	−0·04	56·83	,,
,,	56·52	−0·17	Ag_{5468}	56·69	+0·13	56·82	,,
,,	49·90	−0·21	Hg_{5780}	50·11	−0·22	49·89	,,
,,	48·07	+0·02	Na_{5893}	48·05	+0·15	48·20	,,
,,	44·51	+0·08	Li_{6104}	44·43	+0·23	44·66	,,
,,	39·67	+0·11	Cd_{6438}	39·56	−0·14	39·42	,,
,,	36·22	+0·01	Li_{6709}	36·21	−0·02	36·19	,,

No mutarotation.

TABLE VII. *Camphoric Acid in Ethyl Alcohol.*

$$[\alpha] = \frac{15{\cdot}20}{\lambda^2 - 0{\cdot}0287}\,;\ \lambda_0 = 0{\cdot}1694$$

Dextro			Line λ	Calc. $[\alpha]$ $=c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ $=o$	$o-c$			$o'-c$	Obs. $[\alpha]$ $=o'$	Concentration g./100 c.c.
5·2530	+94·41°	+0·21°	Hg_{4358}	±94·20°	+0·67°	−94·87°	5·2500
,,	66·24	+0·14	Cd_{5086}	66·10	−0·18	65·92	,,
,,	62·63	±0·00	Ag_{5209}	62·63	+0·23	62·86	,,
,,	56·35	+0·14	Hg_{5461}	56·21	−0·02	56·19	,,
,,	56·15	−0·06	Ag_{5468}	56·21	−0·02	56·19	,,
,,	49·68	−0·06	Hg_{5780}	49·74	−0·03	49·71	,,
,,	47·79	+0·07	Na_{5893}	47·72	+0·08	47·80	,,
,,	43·97	−0·23	Li_{6804}	44·20	−0·05	44·15	,,
,,	39·41	+0·13	Cd_{6438}	39·28	+0·13	39·41	,,
,,	35·98	−0·09	Li_{6709}	36·07	+0·25	35·82	,,

No mutarotation.

TABLE VIII. *Camphoric Acid in Ethyl Alcohol.*

$$[\alpha] = \frac{15{\cdot}88}{\lambda^2 - 0{\cdot}0331}\,;\ \lambda_0 = 0{\cdot}1819$$

Dextro			Line λ	Calc. $[\alpha]$ $=c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ $=o$	$o-c$			$o'-c$	Obs. $[\alpha]$ $=o'$	Concentration g./100 c.c.
7·2500	+96·37°	+1·47°	Hg_{4358}	±94·90°	−0·14°	−94·76°	7·2507
,,	66·00	+0·06	Cd_{5086}	65·94	−0·01	65·93	,,
,,	62·40	−0·06	Ag_{5209}	62·46	+0·04	62·50	,,
,,	56·21	+0·09	Hg_{5461}	56·12	±0·00	56·12	,,
,,	55·86	−0·10	Ag_{5468}	55·96	−0·18	55·78	,,
,,	49·38	−0·05	Hg_{5780}	49·43	−0·05	49·38	,,
,,	47·44	+0·05	Na_{5893}	47·39	−0·01	47·38	,,
,,	43·79	−0·04	Li_{6104}	43·83	−0·18	43·65	,,
,,	39·03	+0·02	Cd_{6438}	39·01	+0·23	39·24	,,
,,	35·72	+0·03	Li_{6709}	35·69	−0·03	35·66	,,

No mutarotation.

TABLE IX. *Camphoric Acid in Ethyl Alcohol.*

$$[\alpha] = \frac{14 \cdot 99}{\lambda^2 - 0 \cdot 0289}\ ;\ \lambda_0 = 0 \cdot 1700$$

Dextro			Line λ	Calc. $[\alpha]$ $=c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ $=o$	$o-c$			$o'-c$	Obs. $[\alpha]$ $=o'$	Concentration g./100 c.c.
9·2500	+93·30°	+0·25°	Hg_{4358}	±93·05°	..	..	9·2480
,,	65·21	−0·03	Cd_{5086}	65·24	−0·01°	−65·23°	,,
,,	62·03	+0·19	Ag_{5209}	61·84	+0·15	61·99	,,
,,	55·40	−0·25	Hg_{5461}	55·65	−0·19	55·46	,,
,,	55·49	±0·00	Ag_{5468}	55·49	−0·08	55·41	,,
,,	48·91	−0·20	Hg_{5780}	49·11	−0·03	49·08	,,
,,	46·95	−0·16	Na_{5893}	47·11	−0·09	47·02	,,
,,	43·71	+0·10	Li_{6104}	43·61	+0·17	43·78	,,
,,	39·06	+0·19	Cd_{6438}	38·87	+0·10	38·97	,,
,,	35·62	−0·07	Li_{6709}	35·69	−0·13	35·56	,,

No mutarotation.

TABLE X. *Camphoric Acid in Water.*

$$[\alpha] = \frac{9 \cdot 70}{\lambda^2 - 0 \cdot 1054}\ ;\ \lambda_0 = 0 \cdot 3264$$

Dextro			Line λ	Calc. $[\alpha]$ $=c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ $=o$	$o-c$			$o'-c$	Obs. $[\alpha]$ $=o'$	Concentration g./100 c.c.
0·5055	+62·31°	−0·98°	Cd_{5086}	±63·29°	+0·08°	−63·37°	0·5050
,,	58·36	−0·11	Ag_{5209}	58·47	+1·01	59·46	,,
,,	50·44	+0·13	Hg_{5461}	50·31	+1·17	51·48	,,
,,	51·43	+1·22	Ag_{5468}	50·21	+1·27	51·48	,,
,,	43·52	+1·11	Hg_{5780}	42·41	+1·25	43·66	,,
,,	39·56	−0·59	Na_{5893}	40·15	−0·55	39·60	,,
,,	36·59	+0·28	Li_{6104}	36·31	+0·32	36·63	,,
,,	28·68	+0·53	Li_{6709}	28·15	+1·55	29·70	,,

No mutarotation.

TABLE XI.

Sodium Camphorate in Water.

$$[\alpha] = \frac{6{\cdot}746}{\lambda^2 - 0{\cdot}0106}\,;\ \lambda_0 = 0{\cdot}1029$$

Dextro			Line λ	Calc. $[\alpha]=c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]=o$	$o-c$			$o'-c$	Obs. $[\alpha]=o'$	Concentration g./100 c.c.
5·0060	+27·14°	−0·05°	Cd_{5086}	±27·19°	−0·28°	−26·91°	5·005
,,	25·71	−0·17	Ag_{5209}	25·88	−0·31	25·57	,,
,,	23·46	±0·00	Hg_{5461}	23·46	−0·09	23·37	,,
,,	20·87	+0·02	Hg_{5780}	20·85	+0·02	20·87	,,
,,	20·05	±0·00	Na_{5893}	20·05	+0·13	20·18	,,
,,	18·69	+0·05	Li_{6104}	18·64	±0·00	18·64	,,
,,	16·81	+0·11	Cd_{6438}	16·70	−0·02	16·68	,,
,,	15·52	+0·17	Li_{6709}	15·35	+0·02	15·37	,,

No mutarotation.

TABLE XII.

Camphoric Anhydride in Ethyl Alcohol.

Dextro		Line λ	*Lævo*	
Concentration g./100c.c.	Obs. $[\alpha]=o$		Obs. $[\alpha]=o'$	Concentration g./100 c.c.
0·910	+0·0°	Hg_{4358}	−0·0°	0·960
,,	0·0	Hg_{5461}	0·0	,,
,,	0·0	Hg_{5780}	0·0	,,
,,	0·0	Na_{5893}	0·0	,,
,,	0·0	Li_{6104}	0·0	,,
,,	0·0	Li_{6709}	0·0	,,

TABLE XIII.

Camphoric Anhydride in Chloroform.

Dextro		Line λ	*Lævo*	
Concentration g./100c.c.	Obs. [α]=o		Obs. [α]=o'	Concentration g./100c.c.
4·0316	+0·0°	Hg_{4358}	−0·0°	4·0250
,,	0·0	Hg_{5461}	0·0	,,
,,	0·0	Hg_{5780}	0·0	,,
,,	0·0	Na_{5893}	0·0	,,
,,	0·0	Li_{6104}	0·0	,,
,,	0·0	Li_{6709}	0·0	,,

TABLE XIV.

l-*Borneol in Benzene.*

Concentration : 6·9010 g./100 c.c.

Line λ	Hg_{4358}	Ag_{5209}	Hg_{5461}	Hg_{5780}	Na_{5893}	Li_{6104}	Cd_{6438}	Li_{6709}
Obs.[α]	−77·09°	−50·28°	−45·21°	−39·70°	−38·11°	−35·13°	−31·88°	−29·34°

TABLE XV.

l-*Borneol in Ethyl Alcohol.*

Concentration : 10·6015 g./100 c.c.

Line λ	Hg_{4358}	Cd_{5086}	Ag_{5209}	Hg_{5461}	Hg_{5780}	Na_{5893}	Li_{6104}	Cd_{6438}	Li_{6709}
Obs. [α]	−74·90°	−51·71°	−49·24°	−43·45°	−38·25°	−36·42°	−33·82°	−30·28°	−27·64°

TABLE XVI. *Camphorimide in Ethyl Alcohol.*

$$[\alpha] = \frac{2 \cdot 283}{\lambda^2 - 0 \cdot 0976}; \quad \lambda_0 = 0 \cdot 3124$$

Dextro			Line λ	Calc. $[\alpha]$ $=c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ $=o$	$o-c$			$o'-c$	Obs. $[\alpha]$ $=o'$	Concentration g./100 c.c.
2·1320	+13·84°	−0·33°	Cd_{5085}	±14·17°	−0·09°	−14·08°	2·1307
,,	13·13	−0·01	Ag_{5209}	13·14	±0·00	13·14	,,
,,	11·26	−0·12	Hg_{5461}	11·38	−0·12	11·26	,,
,,	9·61	−0·04	Hg_{5780}	9·65	−0·27	9·38	,,
,,	9·15	±0·00	Na_{5893}	9·15	±0·00	9·15	,,
,,	8·44	+0·14	Li_{6103}	8·30	−0·09	8·21	,,
,,	7·52	+0·32	Cd_{6438}	7·20	+0·07	7·27	,,
,,	6·80	+0·32	Li_{6709}	6·48	+0·56	7·04	,,

No mutarotation.

TABLE XVII. *Camphorimide in Benzene.*

$$[\alpha] = \frac{0 \cdot 68}{\lambda^2 - 0 \cdot 1435}; \quad \lambda_0 = 0 \cdot 3788$$

Dextro			Line λ	Calc. $[\alpha]$ $=c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ $=o$	$o-c$			$o'-c$	Obs. $[\alpha]$ $=o'$	Concentration g./100 c.c.
3·3707	+5·93°	+0·03°	Cd_{5085}	±5·90°	−0·12°	−5·78°	3·3733
,,	5·64	+0·31	Ag_{5209}	5·33	−0·14	5·19	,,
,,	4·30	−0·10	Hg_{5461}	4·40	+0·20	4·60	,,
,,	3·56	−0·01	Hg_{5780}	3·57	−0·01	3·56	,,
,,	3·26	−0·08	Na_{5893}	3·34	+0·07	3·41	,,
,,	2·97	±0·00	Li_{6103}	2·97	+0·14	3·11	,,
,,	2·52	+0·01	Cd_{6438}	2·51	−0·14	2·37	,,
,,	2·23	+0·01	Li_{6709}	2·22	+0·15	2·37	,,

No mutarotation.

TABLE XVIII.

Camphorimide in Chloroform.

$$[\alpha] = \frac{1\cdot708}{\lambda^2 - 0\cdot0555}; \quad \lambda_0 = 0\cdot2355$$

Dextro			Line λ	Calc. $[\alpha]$ $=c$	*Lævo*		
Concentration g./100 c.c.	Obs. $[\alpha]$ $=o$	$o-c$			$o'-c$	Obs. $[\alpha]$ $=o'$	Concentration g./100 c.c.
3·4000	+4·41°	+0·09°	Li_{6708}	±4·32°	+0·09°	−4·41°	3·4033
,,	4·71	−0·05	Cd_{6438}	4·76	−0·21	4·55	,,
,,	5·29	−0·10	Li_{6103}	5·39	−0·25	5·14	,,
,,	5·74	−0·12	Na_{5893}	5·86	+0·02	5·88	,,
,,	6·18	+0·05	Hg_{5780}	6·13	−0·10	6·03	,,
,,	6·91	−0·13	Hg_{5460}	7·04	−0·01	7·03	,,
,,	8·09	+0·17	Ag_{5209}	7·92	+0·01	7·93	,,
,,	8·53	+0·12	Cd_{5085}	8·41	−0·03	8·38	,,

No mutarotation.

A REMARKABLE PROPERTY OF THE "SINGULAR SERIES" IN WARING'S PROBLEM AND ITS RELATION TO HYPOTHESIS K OF HARDY AND LITTLEWOOD.*

By S. Chowla,
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Received September 24, 1935.

§1. Let n be a positive integer $\geqslant 5$. Let ρ denote a primitive qth root of unity. We write

$$S_\rho = \sum_{h=0}^{q-1} \rho^{h^n} = \sum_{h=0}^{q-1} e^{2\pi i \frac{a}{q} h^n}$$

where $(a, q) = 1$. Further

$$A(q) = A(N, n, q, s) = q^{-s} \sum_{\rho} e^{-2\pi i \frac{a}{q} N} (S_\rho)^s$$

where ρ runs over the $\phi(q)$ primitive qth roots of unity [$\phi(q)$ is Euler's totient function]. The "singular series" under consideration is for $s \geqslant 5$,

$$S(N) = S(N; n; s) = \sum_{q=1}^{\infty} A(q) = \prod_{p} \chi_p$$

where p runs through all primes and

$$\chi_p = 1 + A(p) + A(p^2) + \cdots$$

We shall show that

Theorem 1.

$$S(N, n; n + 1) \neq O(1)$$

i.e., for fixed n *and an arbitrary* A *we can find infinitely many positive integers* N *such that*

$$(1) \quad S(N, n; n + 1) > A.$$

In fact we prove that *the number of numbers* $N \leqslant x$ *with the property* (1) *is greater than* Cx (*for large* x), *where* $C = C(A, n)$ *is a positive constant depending only on* A *and* n.

Let $r_{s,n}(N)$ denote the number of representations of N as a sum of s nth powers $\geqslant 0$. Then the last result helps us to show that

Theorem 2.

$$r_{n,n}(N) \neq O(1)$$

i.e., for fixed n *and an arbitrary* A *we can find infinitely many* N *such that* $r_{n,n}(N) > A$.

---

* Dedicated to my friend Sivasankaranarayana Pillai.

Theorem 2 gives us some idea of the behaviour of $r_{n,n}(N)$ for large N. An opposite kind of result is the famous unproved

Hypothesis K. $r_{n,n}(N) = O(N^{\epsilon})$ *for any* $\epsilon > 0$.

In what follows the numbers c (or c_1, c_2, etc.) denote positive constants which depend only on n.

§2. Let us assume the existence of a $c = c(n)$ such that

(I) $r_{n,n}(N) < c$.

If (I) is true, then clearly

(II) $r_{n+1,n}(N) < cN^{\frac{1}{n}}$

since (I) is true, Hypothesis K is true. On the latter assumption we have (from Hardy-Littlewood's P.N. VI in *Math. Ztschr.*, Vol. 23)

(2) $r_{n+1,n}(N) = E\,N^{\frac{1}{n}}S(N\,;\,n\,;\,n+1) + \sigma(N)$

where

(3) $\sum_{m \leqslant x} [\sigma(m)]^2 = O(x^{1+\frac{2}{n}-c})$

and E is a positive constant involving only on n.
From (2) and (3) it follows that

(4) $r_{n+1,n}(N) = E\,S\,(N;\,n\,;\,n+1)\,N^{\frac{1}{n}} + o(N^{\frac{1}{n}})$

is true for " almost all " N.

§3. *Notation.*

$a|b$

means that a is a divisor of b ; $a \nmid b$ is the negation of $a|b$.

$p^{\theta} \parallel m$

means that $p^{\theta}|m$ but $p^{\theta+1} \nmid m$.
$M(p^l) = M(p^l, N)$ is the number of solutions of $h_1^n + \cdots + h_s^n \equiv N \pmod{p^l}$ where $0 \leqslant h_m < p^l$. Clearly $M(p^l, N) > 0$ if $N \equiv 1 \pmod{p^l}$.

The first six of the lemmas below are from Landau's *Vorlesungen uber Zahlentheorie*, Band 1, pages 284, 294, 297, 297, 302, 281 respectively.

Lemma 1. *Let* $p^{\beta n+\sigma} \parallel N$ *where* $\beta \geqslant 0$, $0 \leqslant \sigma < n$; *let* $p^{\theta} \parallel n$ *and* $\gamma = \theta+1$ if $p > 2$, $\gamma = \theta+2$ *if* $p=2$. *Then* $A(p^l) = 0$ *for* $l > l_0$ *where*

$l_0 = \mathrm{Max}\,(\beta n + \sigma + 1,\ \beta n + \gamma)$.

Lemma 2. *If* $q = p^l$, $p \nmid n$, $2 \leqslant l \leqslant n$ *then*

$S\rho = p^{l-1}$

Lemma 3. *If* $q = p$,

$|S\rho| \leqslant (n-1)\sqrt{p}$.

Lemma 4. *For* $q = p^l$, $l > n$, *we have*

$$S_\rho = p^{n-1}\, S_{\rho^{p^n}}$$

(clearly, ρ^{p^n} is a primitive p^{l-n}th root of unity)

Lemma 5. *For* $p > c_1$, $s = n + 1$ $(n \geqslant 4)$

$$\chi_p > 1 - p^{-\frac{5}{4}}$$

Lemma 6.

$$1 + A(p) + A(p^2) + \cdots + A(p^l) = p^{-(s-1)l}\, M(p^l, N).$$

§4. Let p_r denote the rth prime. In the sequel we shall employ the above lemmas only in the case $s = n + 1$.

Lemma 7. *We can find a number* z_1 *so large that* $(p_r, n) = 1$ *for all* $r \geqslant z_1$ *and further,*

$$\chi_{p_r} = 1 + \frac{1}{p_r} + \frac{b}{p_r^{\frac{3}{2}}}\ (n \geqslant 5) \qquad (|b| < 1)$$

for all $r \geqslant z_1$, *where* N *is such that*

$$p_r^n \mid N \qquad (r \geqslant z_1).$$

Proof.—Since $r \geqslant z_1$, p_r is prime to n for sufficiently large z_1 and it follows from lemma 1 that

$$(5)\quad \chi_{p_r} = 1 + A(p_r) + A(p_r^2) + \cdots + A(p_r^{n+1}).$$

From lemma 2,

$$(6)\quad S_\rho(q = p_r^m,\ 2 \leqslant m \leqslant n) = p_r^{m-1},$$

$$(7)\quad (S_\rho)^{n+1} = p_r^{m(n+1)-n-1},$$

$$(8)\quad \rho^{-N} = 1,$$

$$(9)\quad A(q) = \frac{1}{q^{n+1}} \sum_\rho (S_\rho)^{n+1} \rho^{-N}$$
$$= (p_r^m - p_r^{m-1}) p_r^{-n-1}$$
$$= p_r^{m-n-1} - p_r^{m-n-2} \qquad (2 \leqslant m \leqslant n).$$

From (5) and (9),

$$(10)\quad \chi_{p_r} = 1 + \frac{1}{p_r} - \frac{1}{p_r^n} + A(p_r) + A(p_r^{n+1}).$$

By lemma 3,

$$(11)\quad A(p_r) \leqslant \frac{c}{p_r^{n+1}}\, p_r^{\frac{n+1}{2}}\, p_r = \frac{c}{p_r^{\frac{n+1}{2}-1}} = \frac{c}{p_r^2}$$

for $n \geqslant 5$; by lemmas 3 and 4,

$$(12)\quad A(p_r^{n+1}) \leqslant c\, \frac{(p_r^{n-\frac{1}{2}})^{n+1} p_r^{n+1}}{p_r^{(n+1)\left(\frac{n}{2}\right)}}$$

$$= \frac{c}{p_r^{\frac{n}{2}+\frac{1}{2}}} = \frac{c}{p_r^2}\ (n \geqslant 3).$$

From (10), (11), (12),

$$(13)\quad \chi_{p_r} = 1 + \frac{1}{p_r} + \frac{c\,\theta}{p_r^2} \qquad (\text{where } |\theta| < 1)$$

$$= 1 + \frac{1}{p_r} + \frac{b}{p_r^{\frac{3}{2}}} \qquad (\text{where } |b| < 1)$$

for $r \geqslant z_1 = z_1(n)$.

Lemma 8. *Let* $p_1 = 2, p_2, p_3, \cdots, p_m$ $(m = z_1 - 1)$ *be the primes below* p_{z_1}. *Hence* m *depends only on* n. *Let*

$$p_v^{\theta_v} \parallel n \qquad (1 \leqslant v \leqslant m).$$

Let $N \equiv 1 \pmod{Y}$ *where* $Y = 2^{\theta_1+2} \prod_{2 \leqslant v \leqslant m} (p_v^{1+\theta_v})$.

Then[1]

$$\prod_{r \leqslant m} \chi_{p_r} > c > 0.$$

(c *depends only on* n).

Proof. For $2 \leqslant v \leqslant m$ it follows from lemma 1, that

$$(14)\quad \chi_2 = 1 + A(2) + \cdots + A(2^{\theta_1+2}),$$

$$(15)\quad \chi_{p_v} = 1 + A(p_v) + \cdots + A(p_v^{1+\theta_v}).$$

Hence from lemma 6,

$$(15)\quad \chi_2 = 2^{-(\theta_1+2)n}\, M(2^{\theta_1+2}, N).$$

$$(16)\quad \chi_{p_v} = p_v^{-(1+\theta_v)n}\, M(p_v^{1+\theta_v}, N).$$

Since $N \equiv 1 \pmod{2^{\theta_1+2}\, 3^{\theta_2+1} \cdots p_m^{1+\theta_m}}$ we have

$$(17)\quad M(2^{\theta_1+2}, N) \geqslant 1,\ M(p_v^{1+\theta_v}, N) \geqslant 1.$$

Lemma 8 follows from (15), (16), (17) since $\theta_1, \cdots, \theta_m$ depend only on n.

§5. Let A be any preassigned (large) number (it is to be remembered that n is fixed throughout this paper). It follows from lemma 7 that we can find z_2 so large that

$$(18)\quad \prod_{z_1 \leqslant r \leqslant z_2} \chi_{p_r} > A$$

where N satisfies the condition

$$p_r^n \parallel N \quad \text{for } z_1 \leqslant r \leqslant z_2.$$

We may also suppose that $z_2 > c_1$.

Then it follows from lemmas 7, 8 and 5 that

$$(19)\quad S(N; n, n+1) = \prod_{r<z_1} \chi_{p_r} \prod_{z_1 \leqslant r \leqslant z_2} \chi_{p_r} \prod_{r>z_2} \chi_{p_r}$$

$$> c.A.c. = cA$$

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[1] See I. Chowla, "Vinogradow's Solution of Waring's Problem and Hypothesis K of Hardy and Littlewood" to appear in these *Proceedings*.

(by applying lemma 5, since $z_2 > c_1$, to the third product in (19)), where N is restricted by the conditions

$$(20) \quad N \equiv 1 (\mathrm{mod}\ 2^{\theta_1+2} p_2^{\theta_2+1} \cdots p_m^{\theta_m+1})$$

and

$$(21) \quad p_r^n \| N \quad \text{for } z_1 \leqslant r \leqslant z_2.$$

It is clear that for given n and A there is a finite proportion of numbers N satisfying (20) and (21), *i.e.*, the number of solutions of (20), (21) and

$$(22) \quad N \leqslant x$$

is greater than $d\,x$ (for large x) where d is positive and depends only on A and n. Hence we have

Theorem 3. *Let* n *be a fixed integer* $\geqslant 5$. *Let* A *be an arbitrarily large number. Then we can find a positive number* d, *depending only on* A *and* n, *such that the number of solutions* (*in* N) *of*

$$S(N; n; n+1) > A,$$

$$1 \leqslant N \leqslant x,$$

is greater than d x *for large* x.

From Theorem 3, and (4) which is true for almost all N, we easily deduce that

Theorem 4. *Let* $n \geqslant 5$ *be fixed. Let* A *be arbitrarily large. Then if Hypothesis K is true there exists a number* $d = d(A, n) > 0$ *such that the number of solutions* (*in* N) *of*

$$(23) \quad r_{n+1,n}(N) > A N^{\frac{1}{n}}$$

and $1 \leqslant N \leqslant x$

is greater than d x *for large* x.

Now if (I) were true, then (II) would be true. Further Hypothesis K would be true since (I) is supposed true, and hence by Theorem 4, there would be infinitely many N satisfying (23), which contradicts (II). Hence (I) is false and Theorem 2 is true.

Note.—Results similar to Theorem 2, *e.g.*, that $r'_{k,k}(N) \geqslant 2$ for infinitely many $N (3 \leqslant k \leqslant 9)$ where $r'_{k,k}(m)$ is the number of distinct and primitive representations (permutation of the bases not allowed) of m as a sum of k kth powers $\geqslant 0$, have been proved by Wright in his paper "On Sums of kth Powers," *Jour. London Math. Soc.*, 1935, **10**, 94-99.

THE CONDENSATION OF ALDEHYDES WITH MALONIC ACID IN THE PRESENCE OF ORGANIC BASES.

Part IV. The Condensation of Piperonal.

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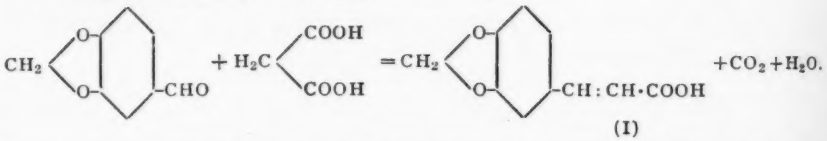
In the condensation of piperonal with malonic acid in the presence of a trace of pyridine,[1] it was found that the yield of the unsaturated acid was highest, *viz.*, 100%. A further study of this has revealed some interesting points.

The product is piperonyl-acrylic acid, (I)



(I)

It was first prepared by Lorenz[2] from piperonal, sodium acetate and acetic anhydride by Perkin's method. He gave the melting-point 232° C. Later on Perkin himself[3] prepared it by a slightly different method, which, he says, "was found to give good yields". Somehow he does not state the actual yields, though he observes that his acid was in every respect identical with that of Lorenz, except in the melting-point, which he found to be higher, namely, 238° C. Dutt[4] reports having prepared it from piperonal, malonic acid and pyridine-piperidine mixture. He, however, does not refer to Lorenz, refers only to Perkin's paper, says that he identified the acid according to Perkin, and yet gives not Perkin's, but Lorenz's figure for the melting-point, *i.e.*, not 238°C., but 232°C. He also reports an yield of 76% by his method. Later on Dutt prepared it again[5] with a molecular proportion of another base, quinoline. The melting-point is not mentioned, but his "best possible yield" was now lower than before, *viz.*, only 60·9%. It was found by Kurien and one of us[6] that with a trace only of pyridine, the yield was theoretical and that the product melted with decomposition at 240°C. In the present paper

it has been found that very careful and repeated purifications raise the melting-point still higher, *viz.*, to 242° C.

The condensations were carried out first with a trace of pyridine—0·15 mol. nearly, and the earlier good yield was confirmed. The following bases were then tried, usually in 0·15 molecular proportion, and the resulting yields varied from 40% to theoretic. In the cases of the lower yields, resin-formation was invariably noticed. It is possible that by varying some of the conditions improvements in the yield might have been seen. But uniform conditions were maintained to make comparisons fair. The bases were :

Lutidine, quinoline, iso-quinoline, quinaldine, diethylaniline, dimethylaniline ; piperidine, methylaniline, ethylaniline, diphenylaniline ; aniline, *o*-toluidine, *m*-toluidine, *p*-toluidine, *α*-naphthylamine, *β*-naphthylamine ; ammonia and ammonium malonate.[6] A very interesting peculiarity is shown by this aldehyde which may throw light on the specific catalytic influence of each of the bases used. Piperonal and malonic acid are found to undergo the same condensation even without the trace of any base. This has indeed been observed, in the case of benzaldehyde by Dutt, as well as by workers in this laboratory. But the product in this case was always the dibasic benzylidene malonic acid. Piperonal, on the other hand, gives the usual monobasic, piperonyl-acrylic acid in a straightforward way. Repeated experiments were made taking every precaution to exclude even a trace of any other substance. Yet the condensation proceeded as usual, and in four hours gave over 50% of piperonyl-acrylic acid. The yield increased on prolonging the heating on the water-bath, and reached the usual theoretical value, about 95% on eighteen hours' heating. Most of the organic bases bring about the same result in 4 hours, and a trace is more effective than a whole molecular proportion, as evidenced by the yields when quinoline and pyridine were used. In other cases resin-production probably not only clogs the reaction but certainly also makes separation less easy and thus diminishes the yield.

Experimental.

The procedure was in all cases very similar to what was found good in earlier condensations. The bases were all purified and generally freshly distilled. The aldehyde was also recrystallised and dried. The malonic acid was Scherring-Kahlbaum's, "pure for scientific purposes," and dried at 100° C. 3 grams piperonal, 2 grams malonic acid and the base in traces as in the Tables, were mixed in a dry flask and heated on a water-bath for about four hours. The aldehyde melted immediately (m.p. 37°C) and the acid gradually dissolved in it. This took about half an hour, after which an evolution of carbon dioxide was

observed, and after about an hour the whole mass in the flask became solid. Heating was continued for three hours more, when it was stopped. On cooling, the mass was taken out, crushed, treated with sodium carbonate solution and warmed. If there was any resinous mass, it was filtered out, and the acid piperonyl-acrylic was separated by the addition of dilute hydrochloric acid. In every case the crude acid was slightly coloured, dirty white, grey or yellow, as was found in earlier cases, by Dutt and by others in this laboratory.

The acid recrystallised from alcohol or acetone melted with decomposition at 242°C. Recrystallisation from glacial acetic acid, or changing into sodium and barium salts and re-precipitating the acid by dilute HCl made no change in the melting-point. The acid was found to be able to undergo sublimation on warming : crystals obtained on sublimation also melted at 242°C.

The equivalent weight of the acid was found

(1) by titration with standard baryta =193,

(2) by the silver salt method=192·4,

while the formula $CH_2 : O_2 : C_6H_3.CH : CH.COOH$ requires 192.

Determination of carbon and hydrogen gave :

Carbon found=62·26%, hydrogen found=4·19%.

The formula $C_{10}H_8O_4$ requires C=62·50%, H=4·16%.

The exact yields with the different bases used are given in the Table at the end.

Condensation without a base.—Malonic acid (2 grams) and piperonal (3 grams) were taken in a flask that was very carefully cleaned and dried. The mixture was heated on the water-bath for different periods, and the product treated as before to separate the acid formed. It was found that with the usual four hours' heating, piperonyl-acrylic acid was formed with 52% yield, and when the heating was prolonged to eighteen hours, the almost theoretical yield of 95% was obtained. The acid was identical in its melting-point to the one obtained before.

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2. Lorenz, *Ber.*, 13, 757.
3. Perkin, *J. C. S.*, 1891, Trans. 152.
4. Dutt, *Jour. Ind. Chem. Soc.*, 1925, **I**, 300.
5. Dalal and Dutt, *Jour. Ind. Chem. Soc.*, 1932, **IX**, 313.
6. According to Knovenagel.

TABLE.

Base	Quantity in c.c.	Approximate in molar proportion	Yield		Remarks: Colour, etc.
			in grams	in %	
Tertiary.					
Pyridine	0·24	0·15	3·4	92	White.
Lutidine	0·34	,,	,,	,,	,,
Quinoline	0·35	,,	3·5	93	Yellowish.
Iso-quinoline	,,	,,	3·6	95	White.
Quinaldine	0·4	,,	3·4	92	Grey, resin.
Diethylaniline ..	0·48	,,	3·2	87	Yellowish, resin.
Dimethylaniline ..	0·37	,,	2·5	67·5	,,
Secondary.					
Piperidine	0·25	0·15	2·5	67·5	White, no resin.
Piperidine	0·5	0·25	3·6	96	,,
Methylaniline ..	0·33	0·15	1·5	40·5	Grey, much resin.
Ethylaniline	0·37	,,	1·7	46	,,
Diphenylamine ..	0·5	,,	2·0	52·6	White, much resin.
Primary.					
Aniline	0·27	0·15	2·1	56·7	Grey, some resin.
o-Toluidine	0·32	,,	2·9	78·0	,,
p-Toluidine	,,	,,	,,	,,	,,
m-Toluidine	,,	,,	2·8	75·6	,,
α-Naphthylamine ..	0·43 gram.	,,	3·0	80·0	Yellowish, resin.
β-Naphthylamine ..	,,	,,	3·2	87·0	,,
Ammonium hydroxide..	0·1 c.c.	,,	2·7	73·0	White, no resin.
Ammonium malonate ..	0·4 gram.	,,	,,	,,	,,

THE DIFFRACTION OF LIGHT BY HIGH FREQUENCY SOUND WAVES: PART I.

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1. *Introduction.*

As is well known, Langevin showed that high frequency sound-waves of great intensity can be generated in fluids by the use of piezo-electric oscillators of quartz. Recently, Debye and Sears[1] in America and Lucas and Biquard[2] in France have described very beautiful experiments illustrating the diffraction of light by such high-frequency sound-waves in a liquid. Amongst the experimenters in this new field, may be specially mentioned R. Bär[3] of Zürich who has carried out a thorough investigation and has published some beautiful photographs of the effect. The arrangement may be described briefly as follows. A plane beam of monochromatic light emerging from a distant slit and a collimating lens is incident normally on a cell of rectangular cross-section and after passing through the medium emerges from the oppsite side. Under these conditions, the incident beam will be undeviated if the medium be homogeneous and isotropic. If, however, the medium be traversed by high-frequency sound-waves generated by introducing a quartz oscillator at the top of the cell, the medium becomes stratified into parallel layers of varying refractive index. Considering the case in which the incident beam is parallel to the plane of the sound-waves, the emerging light from the medium will now consist of various beams travelling in different directions. If the inclination of a beam with the incident light be denoted by θ, it has been found experimentally that the formula

$$\sin\theta = \pm \frac{n\lambda}{\lambda^*}, \quad n \text{ (an integer)} \geqslant 0 \qquad .. \qquad .. \qquad (1)$$

is in satisfactory agreement with the observed results, where λ and λ^* are the wave-lengths of the incident light and the sound wave in the medium

[1] P. Debye and F. W. Sears, *Proc. Nat. Acad. Sci.* (Washington), 1932, **18**, 409.

[2] R. Lucas and P. Biquard, *Jour. de Phys. et Rad.*, 1932, **3**, 464.

[3] R. Bär, *Helv. Phys. Acta*, 1933, **6**, 570.

respectively. With sound waves of sufficient intensity, numerous orders of these diffraction spectra have been obtained; a wandering of the intensity amongst these orders has also been noticed by Bär[3] when the experimental conditions are varied.

Various theories of the phenomena have been put forward by Debye and Sears,[1] by Brillouin,[4] and by Lucas and Biquard.[2] The former have not presented quantitative results and it is hard to understand from their theory as to why there should be so many orders and why the intensity should wander between the various orders under varying experimental conditions. In Brillouin's theory, the phenomenon is attributed to the reflection of light from striations of the medium caused by the sound waves. We know, however, from the work of Rayleigh that the reflection of light by a medium of varying refractive index is negligible if the variation is gradual compared with the wave-length of light. Under extreme conditions, we might perhaps obtain the Brillouin phenomenon, but the components of reflection should be very weak in intensity compared to the transmitted ones. As one can see later on in this paper, the whole phenomenon including the positions of the diffracted beams and their intensities can be explained by a simple consideration of the transmission of the light beam in the medium. Lucas and Biquard attribute the phenomenon to an effect of mirage of light waves in the medium. In what way the relation (1) enters in their theory is not clear. The wandering of the intensities of the various components observed by Bär has not found explanation in any of the above theories.

We propose in this paper a theory of the phenomenon on the simple consideration of the regular transmission of light in the medium and the phase changes accompanying it. The treatment is limited to the case of normal incidence. The formula (1) has been established in our theory. Also, a formula for the intensities of the various components has been derived. It is found that the above results are in conformity with the experimental results of Bär.[3]

2. Diffraction of light from a corrugated wave-front.

The following theory bears a very close analogy to the theory of the diffraction of a plane wave (optical or acoustical) incident normally on a periodically corrugated surface, developed by the late Lord Rayleigh.[5] He showed therein that a diffraction phenomenon would ensue in which the positions of the various components are given by a formula similar to (1)

[4] L. Brillouin, "La Diffraction de la Lumiere par des Ultra-sons", *Act. Sci. et Ind.*, 1933, 59.

[5] Lord Rayleigh, *Theory of Sound* (Vol. 2), page 89.

and their relative intensities are given by a formula similar to the one we have found.

Consider a beam of light with a plane wave-front emerging from a rectangular slit and falling normally on a plane face of a medium with a rectangular cross-section and emerging from the opposite face parallel to the former. If the medium has the same refractive index at all its points, the incident beam will emerge from the opposite face with its direction unchanged. Suppose we now create layers of varying refractive index in the medium, say by suitably placing a quartz oscillator in the fluid. If the distance between the two faces be small, the incident light could be regarded as arriving at the opposite face with variations in the phase at its different parts corresponding to the refractive index at different parts of the medium. The change in the phase of the emerging light at any of its parts could be simply calculated from the optical lengths found by multiplying the distance between the faces and the refractive index of the medium in that region. This step is justified for $\int \mu(x, y, z) ds$ taken over the actual path is minimum, *i.e.*, it differs from the one taken over a slightly varied hypothetical path by a differential of the second order. So, the incident wave-front becomes a periodic corrugated wave-front when it traverses a medium which has a periodic variation in its refractive index. The origin of the axes of reference is chosen at the centre of the incident beam projected on the emerging face, the boundaries of the incident beam being assumed to be parallel to the boundaries of the face. The X-axis is perpendicular to the sound-waves and the Z-axis is along the direction of the incident beam of light. If the incident wave is given by

$$Ae^{2\pi i\nu t}$$

it will be

$$Ae^{2\pi i\nu \{t - l\mu(x)/c\}}$$

when it arrives at the other face where l, is the distance between the two faces and $\mu(x)$ the refractive index of the medium at a height x from the origin. It is assumed that the radii of curvature of the corrugated wave-front are large compared with the distance between the two faces of the cell. If μ_0 be the refractive index of the whole medium in its undisturbed state, we can write $\mu(x)$ as given by the equation

$$\mu(x) = \mu_0 - \mu \sin \frac{2\pi x}{\lambda^*}$$

ignoring its time variation, μ being the *maximum variation* of the refractive index from μ_0.

The amplitude due to the corrugated wave at a point on a distant screen parallel to the face of the medium from which light is emerging whose join

with the origin has its x-direction-cosine l, depends on the evaluation of the diffraction integral

$$\int_{-p/2}^{p/2} e^{2\pi i\{lx+\mu L \sin(2\pi x/\lambda^*)\}/\lambda}\,dx$$

where p is the length of the beam along the X-axis. The real and the imaginary parts of the integral are

$$\int_{-p/2}^{p/2} \{\cos ulx \cos(v \sin bx) - \sin ulx \sin(v \sin bx)\}dx$$

and

$$\int_{-p/2}^{p/2} \{\sin ulx \cos(v \sin bx) + \cos ulx \sin(v \sin bx)\}dx$$

where $u = 2\pi/\lambda$, $b = 2\pi/\lambda^*$ and $v = u\mu L = 2\pi\mu L/\lambda$.

We need the well-known expansions

$$\cos(v \sin bx) = 2\sum_0^{\infty\prime} J_{2r} \cos 2rbx$$

$$\sin(v \sin bx) = 2\sum_0^{\infty} J_{2r+1} \sin \overline{2r+1}\, bx$$

to evaluate the integrals, where $J_n[= J_n(v)]$ is the Bessel function of the nth order and a dash over the summation sign indicates that the coefficient of J_0 is half that of the others. The real part of the integral is then

$$2\sum_0^{\infty\prime} J_{2r} \int_{-p/2}^{p/2} \cos ulx \cos 2rbx\,dx - 2\sum_0^{\infty} J_{2r+1} \int_{-p/2}^{p/2} \sin ulx \sin \overline{2r+1}\, bx\,dx$$

or

$$\sum_0^{\infty\prime} J_{2r} \int_{-p/2}^{p/2} \{\cos(ul+2rb)x + \cos(ul-2rb)x\}dx$$

$$+ \sum_0^{\infty} J_{2r+1} \int_{-p/2}^{p/2} \{\cos(ul+\overline{2r+1}\, b)x - \cos(ul-\overline{2r+1}\, b)x\}dx$$

Integrating the above, we obtain

$$p\sum_0^{\infty\prime} J_{2r} \left\{ \frac{\sin(ul+2rb)p/2}{(ul+2rb)p/2} + \frac{\sin(ul-2rb)p/2}{(ul-2rb)p/2} \right\}$$

$$+ p\sum_0^{\infty} J_{2r+1} \left\{ \frac{\sin(ul+\overline{2r+1}\, b)p/2}{(ul+2r+1\, b)p/2} - \frac{\sin(ul-\overline{2r+1}\, b)p/2}{(ul-\overline{2r+1}\, b)p/2} \right\} \quad .. \quad (2)$$

The integral corresponding to the imaginary part of the diffraction integral

is zero. One can see that the magnitude of each individual term of (2) attains its highest maximum (the other maxima being negligibly small compared to the highest) when its denominator vanishes. Also, it can be seen that when any one of the terms is maximum, all the others have negligible values as the numerator of each cannot exceed unity and the denominator is some integral non-vanishing multiple of b which is sufficiently large. So the maxima of the magnitude of (2) correspond to the maxima of the magnitudes of the individual terms. Hence the maxima occur when

$$ul \pm nb = 0 \quad n(\text{an integer}) \geqslant 0 \quad .. \quad .. \quad .. \quad .. \quad (3)$$

where n is any even or odd positive integer. The equation (3) gives the directions in which the magnitude of the amplitude is maximum which correspond also to the maximum of the intensity. If θ denotes the angle between such a direction in the XZ-plane along which the intensity is maximum and the direction of the incident light, (3) can be written as

$$\sin\theta = \pm \frac{n\lambda}{\lambda^*} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (4)$$

remembering that $u = 2\pi/\lambda$ and $b = 2\pi/\lambda^*$. This formula is identical with the formula (1) given in the first section. The magnitudes of the various components in the directions given by (4) can be calculated if we know,

$$J_n \text{ or } J_n(v) \text{ or } J_n(2\pi\mu L/\lambda).$$

Thus the relative intensity of the mth component to the nth component is given by

$$\frac{J_m^2(v)}{J_n^2(v)} \quad \text{where } v = 2\pi\mu L/\lambda.$$

In the undisturbed state of the medium there is no variation of the refractive index, *i.e.*, $\mu = 0$. In this case all the components vanish except the zero component for

$$J_m(0) = 0 \text{ for all } m \neq 0 \text{ and } J_0(0) = 1.$$

In the disturbed state, the relative intensities depend on the quantity v or $2\pi\mu L/\lambda$ where λ is the wave-length of the incident light, μ is the maximum variation of the refractive index and L is the path traversed by light in the medium. We have calculated the relative intensities of the various components which are observable for values of v lying between 0 and 8 at different steps (Fig. 1).

Fig. 1 shows that the number of observable components increases as the value of v increases. When $v = 0$, we have only the central component. As v increases from 0, the first orders begin to appear. As v increases still more, the intensity of the central component decreases steadily and the first orders increase steadily in their intensity till they attain maximum intensity when the zero order will nearly vanish and the second orders will have just appeared. As v increases still more, the zero order is reborn and increases

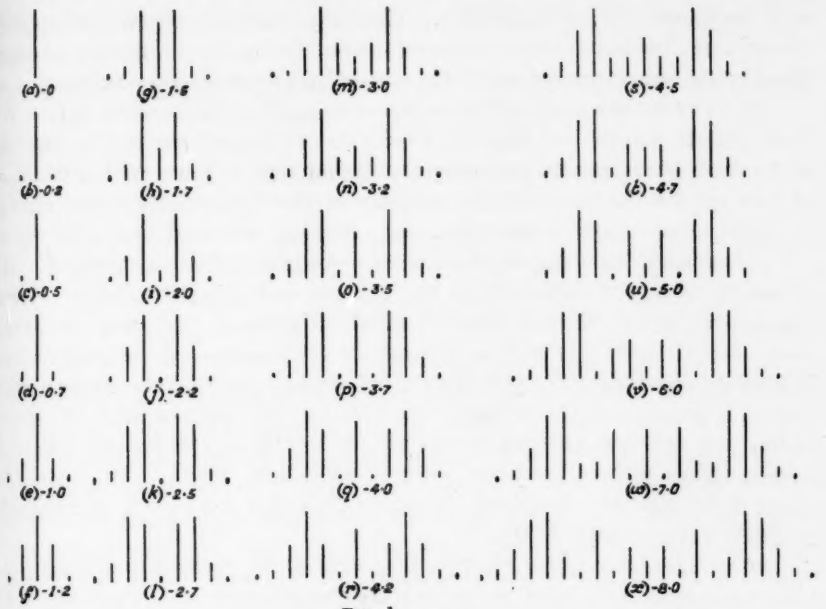

FIG. 1.

Relative intensities of the various components in the diffraction spectra.
(For tables, see Watson's *Bessel Functions and Report of the British Association*, 1915.)

in its intensity, the first orders fall in their intensity giving up their former exalted places to the second orders, while the third orders will have just appeared and so on.

Our theory shows that the intensity relations of the various components depend on the quantity v or $2\pi\mu L/\lambda$. Thus an *increase* of μ (*i.e.*, an increase of the supersonic intensity which creates a greater variation in the refractive index of the medium) or an *increase* of L or a *decrease* of λ should give similar effects *except* in the last case where the directions of the various beams will be altered in accordance with (4).

3. *Interpretation of Bär's Experimental Results.*

(*a*) *Dependence of the effect on the supersonic intensity.*—Bär has observed that only the zero order (strong) and the first orders (faint) are present when the supersonic intensity is not too great. He found that more orders appear as the supersonic intensity is increased but that the intensity of the zero order decreases while the first orders gain in their intensity. Increasing the supersonic intensity more, he found that the first order would become very faint while the second and third orders will have about the same intensity. The figures 1*a* of his paper may very well be compared

with our figures 1(*c*), 1(*h*) and 1(*k*). Thus, we are able to explain the appearance of more and more components and the wandering of the intensity amongst them as the supersonic intensity is increased, in a satisfactory manner.

(*b*) *Dependence of the effect on the wave-length of the incident light.*—We have already pointed out that the effects due to an increase of μ caused by an increase of supersonic intensity are similar due to those with a decrease of λ except for the fact that the positions of the components of the emerging light alter in accordance with (4). Bär has obtained two patterns of the phenomenon by using light with wave-lengths 4750Å and 3650Å. He obtained, using the former seven components and using the latter eleven components in all. He also observed great variations in the intensities of the components. Not only is the increase in the number of components an immediate consequence of our theory, but we can also find the pattern with 3650Å if we assume the pattern with 4750Å. The pattern with the latter in Bär's paper shows a strong resemblance to our figure 1(*p*) for which $2\pi\mu L/\lambda$ is 3·7. Thus we can calculate $2\pi\mu L/\lambda$ when λ is 3650Å. It comes to about 4·8. Actually our figure for which $2\pi\mu L/\lambda$ is 4·8 closely corresponds to Bär's pattern with 3650Å.

(*c*) *Dependence of the effect on the length of the medium which the light traverses.*—It is clear from our theory that an increase of L corresponds to an increase of v and that the effects due to this variation would be similar to those with an increase of the supersonic intensity. But the basis of our theory does not actually cover any large change in L. However, we should find more components and the wandering of the intensity amongst the various components.

4. *Summary.*

(*a*) A theory of the phenomenon of the diffraction of light by sound-waves of high frequency in a medium, discovered by Debye and Sears and Lucas and Biquard, is developed.

(*b*) The formula

$$\sin\theta = \pm\frac{n\lambda}{\lambda^*} \quad n \text{ (an integer)} \geqslant 0$$

which gives the directions of the diffracted beams from the direction of the incident beam and where λ and λ^* are the wave-lengths of the incident light and the sound wave in the medium, is established. It has been found that the relative intensity of the mth component to the nth component is given by

$$J_m^2(2\pi\mu L/\lambda) \;/\; J_n^2(2\pi\mu L/\lambda)$$

where the functions are the Bessel functions of the mth order and the nth order, μ is the maximum variation of the refractive index and L is the path traversed by light. These theoretical results interpret the experimental results of Bär in a very gratifying manner.

THE DIFFRACTION OF LIGHT BY SOUND WAVES OF HIGH FREQUENCY: PART II.

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and
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1. *Introduction.*

In the first[1] of this series of papers, we were concerned with the explanation of the diffraction effects observed when a beam of light traverses a medium filled by sound waves of high frequency. For simplicity, we confined our attention to the case in which a plane beam of light is normally incident on a cell of the medium with rectangular cross-section and travels in a direction strictly perpendicular to the direction along which the sound waves are propagated in the medium. By taking into account the corrugated form of the wave-front on emergence from the cell, the resulting diffraction-effects were evaluated. This treatment will be extended in the present paper to the case in which the light waves travel in a direction inclined at a definite angle to the direction of the propagation of the sound waves. The extension is simple, but it succeeds in a remarkable way in explaining the very striking observations of Debye and Sears[2] who found a characteristic variation of the intensity of the higher orders of the diffraction spectrum when the angle between the incident beam of light and the plane of the sound waves was gradually altered.

We shall first set out a simple geometrical argument by which the changes in the diffraction phenomenon which occur with increasing obliquity can be inferred from the results already given for the case of the normal incidence. An analytical treatment then follows which confirms the results obtained geometrically.

2. *Elementary Geometrical Treatment.*

The following diagrams illustrate the manner in which the amplitude of the corrugation in the emerging wave-front alters as the incidence of light on the planes of the sound waves is gradually changed. In the diagrams,

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[1] C. V. Raman and N. S. Nagendra Nath, *Proc. Ind. Acad. Sci.*, 1935, **2**, 406—412.

[2] P. Debye and F. W. Sears, *Proc. Nat. Acad. Sci.* (Washington), 1932, **18**, 409.

the planes of maximum and minimum density caused by the sound waves at any instant of time are indicated by thick and thin lines (*e.g.*, AB and CD) respectively. The paths of the light rays are represented by dotted lines in Figs. 1 (*b*), (*c*) and (*d*). As we are mainly interested in the calculation of the phase-changes which the incident wave undergoes before it emerges from the cell, the bending of the light rays within the medium may, in virtue of Fermat's well-known principle, be ignored without a sensible error, *provided* the total depth of the cell is not excessive.

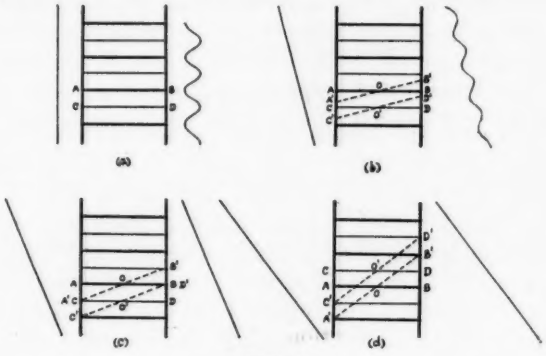

FIG. 1.

Considering the variation in the refractive index to be simply periodic, the neighbouring light-paths with maximum and minimum optical lengths AB and CD respectively, in the case of normal incidence, are shown in Fig. 1(*a*). The lines AB and CD are separated by $\lambda^*/2$ where λ^* is the wave-length of the sound waves. The difference between the maximum and the minimum optical lengths gives a measure of the corrugation of the wave-front on emergence. Considering now a case in which the light rays make an angle ϕ with the planes of the sound waves, we may denote the maximum and the minimum optical lengths by A′B′ and C′D′ respectively. These would be symmetrically situated with respect to AB and CD, and would tend to coincide with them as ϕ is decreased. The optical length of A′B′ is *less* than that of AB, for the refractive index at any point except at O is less than the constant maximum refractive index along AB, ϕ being small. On the other hand, the optical length of C′D′ is *greater* than that of CD, for the refractive index is minimum along CD. A simple consideration of the above shows that the difference between the optical lengths of A′B′ and C′D′ is less than that between those of AB and CD. As this difference gives twice the amplitude of the corrugation of the emerging wave-front, it follows, in the case shown in Fig. 1 (*b*), that the amplitude of the

corrugation of the emerging wave-front is less than that in the case of Fig. 1 (*a*).

Fig. 1 (*c*) illustrates a case when the maximum optical length is just equal to the minimum optical length. This occurs when the direction of the incident beam is inclined to the planes of the sound-wave-fronts at an angle α_1 given by $\tan^{-1}\frac{B'B}{OB} = \tan^{-1}\frac{\lambda^*/2}{L/2} = \tan^{-1}(\lambda^*/L)$. That the optical lengths of A'B' and C'D' in Fig. 1 (*c*) are equal follows by a very simple geometrical consideration. Thus, when light rays are incident on the sound waves at an angle $\tan^{-1}(\lambda^*/L)$, the amplitude of the corrugation of the emerging wave-front vanishes, *i.e.*, a plane incident beam of light remains so when it emerges from the medium. This result would also be true whenever $\alpha_n = \tan^{-1}(n\lambda^*/L)$, $n \neq 0$. The case when $n = 2$ is illustrated in Fig. 1 (*d*). In all these cases the diffraction effects disappear. As the corrugation vanishes when ϕ is α_{n+1} or α_n, there is an intermediate direction which makes an angle β_n with the sound waves giving the maximum corrugation if light travels along that direction. We can take $\beta_0 (= 0)$ to represent the case when the incident beam of light is parallel to the sound waves.

Thus, we have deduced that the corrugation of the emerging wave-front is maximum when the direction of light is parallel to the sound waves $[\beta_0 (= 0)]$, decreases steadily to zero as the inclination ϕ between the incident light and the sound waves is increased to α_1, increases to a smaller maximum as ϕ increases from α_1 to β_1, decreases to zero as ϕ increases from β_1 to α_2, increases to a still smaller maximum as ϕ increases from α_2 to β_2, and so on. (I)

As the variation of the refractive index is simply periodic along the direction normal to the sound-wave-fronts, it follows that the optical length of the light path is also simply periodic along the same direction when the incident light rays are parallel to the sound waves. This means that the corrugation of the emerging wave-front is also simply periodic. When the incident light rays are incident at an angle ϕ to the sound waves, the optical length of the light path would be simply periodic in a direction perpendicular to the light rays. This means that the emerging wave-front would be tilted by the angle ϕ about the line of the propagation of the sound waves and that its corrugation would be simply periodic along the same line.

We have shown in our previous paper that a simply periodic corrugated wave is equivalent to a number of waves travelling in directions which make angles, denoted by θ, with the direction of the incident beam given by

$$\sin\theta = \pm \frac{n\lambda}{\lambda^*} \qquad n \text{ (an integer)} \geqslant 0 \qquad \ldots \qquad \ldots \quad (1)$$

where λ is the wave-length of the incident light. In view of the results obtained in the previous paragraph, the formula (1) would also hold good when the incident light is a small angle with the sound waves.

The relative intensities of the various diffraction spectra which depend on the amplitude of the corrugation should obey a law similar to the one in the case of the normal incidence.

Thus, we find that the results in the case of an oblique incidence would be similar to those of the normal incidence with the amplitude of the corrugation modified. Hence, we deduce, in virtue of the statement I, the following results, assuming the results, in the case of normal incidence, obtained in our earlier paper.

The diffraction spectrum will be most prominent when $\phi = 0$. The intensity of the various components wander when ϕ is increased. When ϕ increases from zero to α_1, the number of the observable orders in practice decreases and when $\phi = \alpha_1$ all the components disappear except the central one which will attain maximum intensity. This does not mean that the intensities of all the orders except the central one decrease to zero monotonically as ϕ varies from zero to α_1, but some of them may attain maxima and minima in their intensities before they attain the zero intensity when $\phi = \alpha_1$. This is obvious in virtue of the property that the intensity of the nth component depends on the square of the Bessel function J_n. As ϕ increases from α_1 to β_1 the intensity of the central component falls and the other orders are reborn one by one. As ϕ increases from β_1 to α_2, the number of observable orders decreases and when $\phi = \alpha_2$ all the orders vanish except the central one which will attain the maximum intensity and so on.

3. *Analytical Treatment.*

In the following, we employ the same notation as in our earlier paper. The optical length of a path in the medium parallel to the direction of the incident light making an angle ϕ with the sound waves may be easily calculated. It is

$$\int_0^{L \sec\phi} \mu(s)ds$$

or

$$\mu_0 L \sec\phi - \mu \int_0^{L \sec\phi} \sin b(x - s\sin\phi)ds.$$

Integrating we obtain the integral as

$$\mu_0 L \sec\phi - \frac{\mu}{b \sin\phi}\{\sin(bL \tan\phi)\sin bx + [\cos(bL \tan\phi) - 1]\cos bx\}.$$

The last term can be written as

$$-A \sin bx + B \cos bx$$

where

$$A = \frac{\mu}{b \sin\phi} \sin(bL \tan\phi)$$

$$B = -\frac{\mu}{b \sin\phi}[\cos(bL \tan\phi) - 1].$$

Thus the optical length of the path can be written as

$$\mu_0 L \sec\phi - \sqrt{(A^2 + B^2)} \sin b\left(x - \tan^{-1}\frac{B}{A}\right).$$

Ignoring the constant phase factor, the optical length is

$$\mu_0 L \sec\phi - \frac{2\mu}{b \sin\phi} \sin\left(\frac{bL \tan\phi}{2}\right) \sin bx.$$

If the incident light is

$$\exp\left[2\pi i\nu\left(t - \frac{x \sin\phi}{c}\right)\right]$$

when it arrives at the face of the cell, it will be

$$\exp\left[\frac{2\pi i}{\lambda}\left(ct - x \sin\phi - \int_0^{L \sec\phi} \mu(s)ds\right)\right]$$

when it arrives at the face from which it emerges.

The amplitude of the corrugated wave at a point on the screen whose join with the origin has its x-direction-cosine l, depends on the evaluation of the diffraction integral

$$\int_{-p/2}^{p/2} \exp\left[\frac{2\pi i}{\lambda}\left\{(l - \sin\phi)x + \frac{2\mu}{b \sin\phi} \sin\left(\frac{bL \tan\phi}{2}\right) \sin bx\right\}\right] dx.$$

The evaluation of the integral and the discussion of its behaviour with respect to l may be effected in the same way as in our earlier paper. Maxima of the intensity due to the corrugated wave occur in directions making angles, denoted by θ, with the direction of the incident beam when

$$\sin(\theta + \phi) - \sin\phi = \pm \frac{n\lambda}{\lambda^*} \qquad n \text{ (an integer)} \geqslant 0 \qquad \ldots\ (1)$$

The relative intensity of the mth order to the nth order is given by

$$\frac{J_m^2(v)}{J_n^2(v)} \qquad \ldots\ (2)$$

where

$$v = \frac{2\pi}{\lambda} \cdot \frac{2\mu}{b \sin \phi} \sin\left(\frac{bL \tan \phi}{2}\right)$$

$$= \frac{2\pi\mu L}{\lambda} \sec \phi \frac{\sin t}{t} \text{ where } t = \frac{bL \tan \phi}{2} = \frac{\pi L \tan \phi}{\lambda^*}.$$

The expression for the relative intensities in our earlier paper can be obtained from (2) by making $\phi \to 0$ when $v \to \frac{2\pi\mu L}{\lambda} = v_0$. So the expression for the relative intensities

$$J_m^2(v_0)/J_n^2(v_0) \quad .. \quad .. \quad .. \quad .. \quad (3)$$

in the case of normal incidence will change to

$$J_m^2(v)/J_n^2(v)$$

where

$$v = v_0 \sec \phi \frac{\sin t}{t} \quad .. \quad .. \quad .. \quad .. \quad (4)$$

and

$$t = \frac{\pi L \tan \phi}{\lambda^*}.$$

Even if ϕ be small so that $\sin \phi \backsimeq \tan \phi \backsimeq \phi$, it is *not* justifiable to write $\sin t \backsimeq t$ *unless* $\pi L\phi/\lambda^*$ is also small to admit the approximation. As $\pi L/\lambda^*$ is sufficiently large we should expect great changes in the diffraction phenomenon even if ϕ be a fraction of a degree. v vanishes when

$$t = n\pi \qquad n \text{ (an integer)} > 0,$$

that is, when $L \tan \phi = n\lambda^*$,

or

$$\phi = \tan^{-1} \frac{n\lambda^*}{L}, \; n \text{ (an integer)} > 0,$$

confirming the same result obtained geometrically. Whenever v vanishes, it can be seen that the amplitude of the corrugation of the wave-front also vanishes. The statement I in Section 2 and the consequences with regard to the behaviour of the intensity among the various orders can all be confirmed by the expression (3).

In the numerical case when $L = 1$ cm., and $\lambda^* = 0{\cdot}01$ cm., the amplitude of the corrugation vanishes $\tan \alpha_1 = 0{\cdot}01$ or $\alpha_1 = 0°\ 34'$. This means that as ϕ varies from 0° to 0° 34′, the relative intensities of the various orders wander according to (2) till when $\phi = 0°\ 34'$, all the orders disappear except the central one which attains maximum intensity. This does not mean that the intensities of all the orders except the central one decrease monotonically to zero but they *may possess* several maxima and minima before they become zero. The intensity of the nth order depends on the behaviour

of $J_n^2\left[v_0 \sec\phi \frac{\sin(\pi L \tan\phi/\lambda^*)}{(\pi L \tan\phi/\lambda^*)}\right]$ under the above numerical conditions as ϕ varies from 0° to 0° 34′. As ϕ just exceeds 0° 34′, all the orders are reborn one by one till a definite value of ϕ after which they again fall one by one and when $\phi = 1°\ 8'$, all the orders disappear except the central one.

The numerical example in the above paragraph shows the delicacy of the diffraction phenomenon. If the wave-length is quite small, the diffraction phenomenon will be present in the case of the strictly normal *incidence* as the relative intensity expression (3) does not depend on λ^* but will soon considerably change even for slight variations of ϕ as the relative intensity expression (4) depends on λ^*. One should be very careful in carrying out the intensity measurements in the case of normal incidence, for even an error of a few minutes of arc in the incidence will affect the intensities of the various orders.

4. Comparison with the experimental results of Debye and Sears.

Debye and Sears make the following statement in their paper: "Fixing the attention on one of the spectra *preferably of higher order*, one can observe that it attains its maximum intensity if the trough is turned through a small angle such that the primary rays are no longer parallel to the planes of the supersonic waves. Different settings are required to obtain highest intensities in different orders. If the trough is turned continuously in one direction, starting from a position which gave the highest intensity to one of the orders, the intensity decreases steadily, goes through zero, increases to a value much smaller than the first maximum, decreases to zero a second time and goes up and down again through a still smaller maximum." This statement very aptly describes the behaviour of the function

$$J_n^2\left[v_0 \sec\phi \frac{\sin(\pi L \tan\phi/\lambda^*)}{(\pi L \tan\phi/\lambda^*)}\right]$$

as ϕ alters under the conditions imposed in the above statement. The zeroes and the maxima of the intensity of the nth order, as a function of ϕ, correspond to the zeroes and the maxima of the above function.

5. Summary.

The theory of the diffraction of light by sound waves of high frequency developed in our earlier paper is extended to the case when the light beam is incident at an angle to the sound wave-fronts, both from a geometrical point of view and an analytical one. It is found that the maxima of intensity of the diffracted light occur in directions which make definite angles, denoted by θ, with the direction of the incident light given by

$$\sin(\theta+\phi) - \sin\phi = \pm \frac{n\lambda}{\lambda^*},\ n \text{ (an integer)} \geqslant 0$$

where λ and λ^* are the wave-lengths of the incident light and the sound waves in the medium. The relative intensity of the mth order to the nth order is given by

$$J_m^2\left(v_0 \sec\phi \frac{\sin t}{t}\right) \Big/ J_n^2\left(v_0 \sec\phi \frac{\sin t}{t}\right)$$

where $v_0 = \frac{2\pi\mu L}{\lambda}$, $t = \frac{\pi L \tan\phi}{\lambda^*}$, ϕ is the inclination of the incident beam of light to the sound waves, μ is the maximum variation of the refractive index in the medium when the sound waves are present and L sec ϕ is the distance of the light path in the medium. These results explain the variations of the intensity among the various orders noticed by Debye and Sears for variations of ϕ in a very gratifying manner.

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ALKALOIDS FROM THE SEEDS OF *CASSIA ABSUS*, LINN.

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Received September 9, 1935.

Cassia absus, Linn. (N. O. Leguminosæ; vernacular, Chaksu) is an erect annual plant, 1 to 2 ft. high, occurring throughout India and Ceylon. Its flat oblong seeds, dark and about 1/10" contain a kernel used in the treatment of ophthalmia and skin affections and as a cathartic.[1]

The presence of an alkaloidal principle in the drug has been previously reported.[2] As a result of the present investigation two water soluble, isomeric quaternary bases have been isolated as carbonates in a total yield of about 1·5 per cent. of the kernel. These bases which the authors propose to call chaksine and isochaksine appear to have the molecular formula $C_{12}H_{21}O_2N_3$ based on the analysis of their salts.

The separation of the bases was facilitated by the sparing solubility of chaksine iodide and sulphate in water and alcohol and of the carbonate in alcohol, the corresponding isochaksine salts being easily soluble. Neither of the bases could be isolated pure owing to the avidity with which they absorb CO_2 from the air, chaksine forming an acid carbonate and isochaksine a neutral carbonate. No indication of isomerisation was noted on long heating of chaksine salts in various solvents but chaksine is partially isomerised when liberated from its iodide and completely converted into isochaksine when its sulphate is treated with barium hydroxide. The alcohol-acetone soluble iodide after separation of chaksine iodide directly gave isochaksine picrate showing isochaksine to be present originally in the seeds and not formed by isomerisation in the process of isolation.

Chaksine iodide appears to have no methoxyl or N-methyl groups. Both the bases are mono-acidic but one of the two remaining nitrogen atoms

[1] Kirtikar and Basu, *Indian Medicinal Plants*, Vol. 1, p. 478.

[2] Dymock, *Pharm. Indica*, Vol. 1, p. 525; also noted in the course of a preliminary examination of the seeds, carried out by one of us (Z. A.) in the Tibbia College, Muslim University, Aligarh.

appears to be mildly basic as the platinum double salts seem to be derived from a chloride hydrochloride ($C_{12}H_{20}ON_3HCl)Cl$. While the Pt. double salt of isochaksine appears to be stable at 120° *in vacuo*, the chaksine salt loses a molecule of HCl from the weaker basic nucleus. Investigation on further elucidation of this point and studies on the two bases will be undertaken after collection of fresh material. Preliminary experiments on the pharmacological action of the bases, with dilute aqueous solution of chaksine sulphate on frogs, show it to be a general depressent of heart, respiration and nerves, the lethal dose in the case of frogs being 0·1 g. per kg.

Experimental.

After a series of preliminary experiments, 3·6 kg. of well-powdered kernel were percolated six times in the cold with 0·3 per cent. methyl alcoholic HCl during a fortnight. The combined percolates were neutralised with ammonia, made acidic with acetic acid, and the alcohol distilled off under reduced pressure below 40°. The brownish yellow, syrupy residue was freed of the oily matter by exhausting it with ether.

Isolation of chaksine and isochaksine iodides.—The residue was freed of ether on the water-bath and taken up in about 2 litres of water, acidified with a little dilute HCl, in which it was completely soluble. Potassium iodide (50 g.) was slowly added when on standing in the cold chaksine iodide separated as a thick whitish crystalline mass, which was sucked in the filter and successively washed with 5 per cent. potassium iodide solution, alcohol, acetone and ether. 30 g. crude iodide thus obtained yielded 25 g. chaksine iodide on crystallisation from a mixture of alcohol and water, the melting point being unaltered on further recrystallisation. The residue from the washings and the alcohol-water mother liquors of the iodide yielded on recrystallisation after charcoaling, a further crop of 12 g. pure chaksine iodide.

The residual base was precipitated from the combined aqueous filtrates and washings from chaksine iodide with an alcoholic solution of mercuric chloride. The thick, dark brown, pasty precipitate was washed with hot water, dissolved in 5 per cent. alcoholic HCl and sulphuretted hydrogen passed through the solution under gradual dilution with water till all the mercury was removed. The filtrate was freed of H_2S, ammoniated, acidulated with acetic acid and concentrated down to a small volume *in vacuo*, the black non-alkaloidal resinous matter, which separated out, being neglected. The clear reddish solution, thus obtained, was charcoaled and cooled, when a fresh crop of pure chaksine iodide (9 g.) was obtained, the total yield of chaksine iodide being 46 g., or 1·3 per cent. of the weight of the kernel.

Further addition of potassium iodide gave a semisolid iodide which was almost completely soluble in acetone containing a little alcohol (about 5 : 100), in which chaksine iodide is insoluble. On purifying this iodide in acetone solution by adding a little ether and petroleum ether to remove any persistent impurity of chaksine iodide and the colouring or resinous matter and removing the solvent from the supernatant solution, isochaksine iodide was obtained as a water and alcohol-acetone soluble, reddish yellow paste which failed to crystallise, its yield being about a tenth of that of chaksine iodide.

In a subsequent working of 2·5 kg. of the kernel, chaksine was separated through its insoluble sulphate by treating the water soluble portion of the methyl alcoholic HCl extract with sodium sulphate, whereby 30 g. crude sulphate (25 g. pure iodide) were obtained, the isochaksine iodide being obtained from the filtrates in the manner detailed above.

Chaksine ($C_{12}H_{21}O_2N_3$) *and chaksine bicarbonate* ($C_{12}H_{20}ON_3HCO_3$).—5·3 g. chaksine iodide were dissolved in 50 c.c. alcohol in the hot and the solution treated with freshly precipitated silver hydroxide from 4·5 g. silver nitrate, filtered, and the residue extracted with hot alcohol. To the slightly greenish yellow filtrate was added an equal volume of ether (200 c.c.) and about 50 c.c. of petroleum ether, the dirty greenish precipitate being redissolved in alcohol and treated with ether-petroleum ether. The precipitate was neglected and the combined filtrates were further purified by addition of a little petroleum ether till a nearly colourless silver-free solution (about 500 c.c.) was obtained which was allowed to evaporate in an open dish. A greenish, crystalline powder was obtained which crystallised out in stars of needles on slow evaporation of an alcoholic solution. It dissolved with frothing in dilute acids and melted at 167–69° with frothing. The alcoholic washings of this crystalline product yielded a further quantity of the same product and an alcohol soluble base forming a greenish sticky residue which was strongly alkaline to litmus in aqueous solution and on rubbing with petroleum ether was converted into an alcohol soluble carbonate which proved to be the normal carbonate of isochaksine, as obtained directly from isochaksine iodide. The air-dried crystalline carbonate of chaksine appeared to contain ½ a molecule of water. (Found : C, 53·38 ; H, 8·15 ; N, 14·58 ; $C_{12}H_{20}ON_3.HCO_3 + \frac{1}{2}\ H_2O$ requires C, 53·42 ; H, 7·54 ; N, 14·54 per cent.) On heating to constant weight at 100° *in vacuo* lost 3·47 per cent. ; required for ½ H_2O, 3·10 per cent. (Found after dehydration : C, 55·06 ; H, 8·12 ; N, 15·31 ; $C_{12}H_{20}ON_3.HCO_3$ requires C, 55·12 ; H, 7·42 ; N, 14·84 per cent.)

When chaksine is liberated from its iodide in aqueous solution or alcohol and the solvent is removed in vacuum the base is obtained as a reddish treacle soluble in water and alcohol, difficultly soluble in acetone, insoluble

in ether and petroleum ether. This product, however, was contaminated with silver to the extent of about 5 per cent., was not completely free of chaksine carbonate and apparently also contained some isomerised chaksine, as the melting point of the picrate from its solution in HCl was about 10° lower than that of pure chaksine picrate. Attempts to isolate the pure base, uniform enough for analysis, did not succeed. In its impure form it had $[a]_D = +32°$ in absolute alcohol (C, 1·0).

Chaksine iodide came out as a thick crystalline precipitate on adding a concentrated solution of KI to a solution of the carbonate in dilute acetic acid. On recrystallisation from absolute alcohol it formed colourless needles, which after drying in vacuum shrink at 150° and melt at 168° (decomp.). After Zeisel's method it was found to contain no methoxyl group. After Herzig and Meyer's method it was found to contain no N-methyl. It is very sparingly soluble in water and alcohol, insoluble in acetone and ether. (Found after drying at 100° *in vacuo:* I, 34·90; $C_{12}H_{20}ON_3I$ requires I, 36·39 per cent.)

Chaksine sulphate was obtained by adding a concentrated solution of sodium sulphate to a solution of the carbonate in dilute acetic acid as a thick, snow-white, crystalline mass. It is sparingly soluble in hot alcohol or water, fairly soluble in saline water or alcohol acidulated with HCl. On recrystallisation from water it forms colourless silky needles, which begin to colour at 290°, shrink at 312° and melt at 316° (decomp.) the m.p. of the sulphate originally obtained from the alcoholic extract of the kernel being 16° lower. [Found after Carius: S, 5·7; by direct precipitation from its aqueous solution with $BaCl_2$, 5·85; $(C_{12}H_{20}ON_3)_2SO_4$ requires S, 5·93 per cent.]

Chaksine picrate was obtained as a bright yellow, crystalline powder on adding aqueous picric acid to a solution of the carbonate in dilute hydrochloric acid. It is very sparingly soluble in water and alcohol, begins to redden and shrink at 225° and melts at 239–40° (decomp.).

The platinum salt of chaksine.—On adding 10 per cent. solution of platinic chloride to a solution of the carbonate in dilute HCl the platinate came out in orange yellow crystalline needles, difficultly soluble in water and melting at 232° (decomp.). After drying at 100° it gave C, 30·66; H, 4·51, N, 9·60; Cl, 30·16; Pt. 21·00; $(C_{12}H_{20}ON_3HCl)_2Cl_2.PtCl_4$ requires C, 31·12; H, 4·35; N, 9·08; Cl, 30·69; Pt, 21·10 per cent. On heating to constant weight at 120° [Found: Pt. 22·60; $(C_{12}H_{20}ON_3)_2Cl_2PtCl_4$ requires Pt, 22·90 per cent.]

Isochaksine, $(C_{12}H_{21}C_2N_3)$ *and isochaksine carbonate* $(C_{12}H_{20}ON_3)_2CO_3$.—On treating an alcoholic solution of isochaksine-iodide with freshly precipitated silver hydroxide and purifying the filtrate with ether and petroleum ether isochaksine was obtained as a cream coloured hygroscopic treacly mass,

easily soluble in water and alcohol and strongly alkaline to litmus. It appears to be less inclined to form a carbonate than chaksine and it took much longer to get converted into uniform carbonate on mere exposure to the air. The carbonate, however, was easily obtained on treating it with petroleum ether saturated with carbon dioxide as an amorphous powder which was easily soluble in cold alcohol, insoluble in ether and petroleum ether, began to sinter at 108° and frothed up at 128°. Isochaksine carbonate was also obtained when chaksine carbonate was heated for about an hour on the water-bath in alcoholic solution. Also, when a solution of chaksine sulphate in methyl alcohol, containing a little dilute sulphuric acid, was treated with barium hydroxide solution and the excess of the hydroxide removed as carbonate, isochaksine carbonate was obtained on removal of the solvent from the final filtrate on the water-bath. In which-ever manner obtained, isochaksine or its carbonate did not yield a crystalline iodide or sulphate which could be characterised through its sparing solubility in water or alcohol. [After drying the carbonate to constant weight at 100° found : C, 58·74 ; H, 8·57 ; N, 16·31 ; $(C_{12}H_{20}ON_3)_2CO_3$ requires C, 59·52 ; H, 7·93 ; N, 16·66 per cent.] A little low carbon value may be due to its contamination with persistent impurities as bicarbonate of chaksine or isochaksine which requires only 55·12 per cent. carbon.

Isochaksine chloride.—On adding ethereal HCl to a solution of the base in a mixture of absolute alcohol and ether, the chloride came out as a colourless oil which on rubbing and washing with dry ether turned into a white, extremely hygroscopic, crystalline powder. It is easily soluble in water and alcohol and after drying in vacuum apparently begins to give off moisture at 90° with frothing, turning into a brittle mass, which melts at 250–52° without reddening. (Found after drying at 100° *in vacuo* : Cl, 13·56 ; $C_{12}H_{20}ON_3Cl$ requires Cl, 13·78 per cent.)

Isochaksine picrate, obtained in the same manner as that of chaksine, was a bright yellow powder melting at 184° as against 230°, noted for chaksine picrate.

Isochaksine platinate, prepared as in case of chaksine, formed an orange-yellow, granular powder, difficultly soluble in water and alcohol. After drying at 100°, it shrinks at 165° and melts with frothing at 172°. [Found after heating to constant weight at 120° *in vacuo :* Pt, 20·95, 21·1 ; $(C_{12}H_{20}ON_3HCl)_2Cl_2.PtCl_4$ requires Pt. 21·1 per cent.]

One of the authors (Z. Ahmed) takes this opportunity to thank the authorities of the Tibbia College, Muslim University, Aligarh, for the grant of a scholarship, which enabled him to take part in these investigations.

STUDIES IN THE CONESSINE SERIES.

Part I. Isomerisation of Conessine and its Nor-Bases.

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In a series of communications[1] on the alkaloids of Holarrhena Antidysenterica the author and his collaborators have dealt at length with the isolation of a number of subsidiary alkaloids of conessine from the bark and the seeds of the Indian Holarrhena, and largely cleared up the confusion existing about their uniformity and chemical character by establishing the mutual relationship between the non-oxygenous bases of the plant. Further studies by the author in the same problem have led to the conclusion that all the alkaloids of the plant bear a simple relationship to conessine, $C_{21}H_{31}{}^{:N-CH_3}_{:N-(CH_3)_2}$, most of them differing from it only in the number and position of N-methyls in their molecules. In view of these findings, which would be shortly communicated, the investigations in the alkaloids of the plant take on a new aspect and are virtually simplified to studies in the molecule of the chief alkaloid, conessine, which has now become easily accessible owing to the enormous increase in its yield (from 0·1 to 0·8% approximately) through the direct methylation of the mixture of secondary bases occurring in the plant. The author consequently started a fresh series of investigations aiming at a deeper insight into the molecule of conessine from various standpoints. The present paper, which is the first of this series, deals with the isomerisation of conessine and its nor-bases, isoconessimine, ($C_{23}H_{38}N_2$), and conimine, ($C_{22}H_{36}N_2$), effected through the action of concentrated sulphuric acid on the corresponding bases in the cold.

Warnecke[2] noted that conessine dissolves to a colourless solution in sulphuric acid (conc.) which on warming or long standing turns bright yellow and then green, and on subsequent slow absorption of moisture (or gradual addition of water) becomes dark blue and finally bright violet. This colour

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[1] S. Siddiqui and P. P. Pillay, *J. Indian Chem. Soc.*, 1932, **9**, 553.
S. Siddiqui, *J. Indian Chem. Soc.*, 1934, **11**, 283–91.
S. Siddiqui and R. H. Siddiqui, *J. Indian Chem. Soc.*, 1934, **11**, 787.

[2] Warnecke, *Ber.*, 1886, **19**, 60.

reaction was confirmed by the subsequent authors[3] who studied the reaction as a characteristic of conessine. At the same time Warnecke observed that oxy-conessine, which he obtained through the action of iodic acid on conessine, directly dissolved in sulphuric acid to a yellow solution, which quickly turned yellowish green and finally deep red. Taking into consideration the comparative behaviour of conessine and oxy-conessine in H_2SO_4 and on the basis of his own observations in this colour reaction in the case of conessine and the secondary bases isolated by the author (*loc. cit.*), it appeared very likely that the sequence of colours noted on solution of the non-oxygenous bases of the series and gradual addition of water to the solution was due to a process of gradual oxidation. That Giemsa and Halberkann (*loc. cit.*) had later on succeeded in oxidising oxy-conessine with a mixture of 20% sulphuric acid and chromic acid to what they considered to be an amino acid answering to the formula $C_{22}H_{33}NO_4$, lent further support to this view.

A careful study of the action of sulphuric acid on conessine under varying conditions of temperature, time of reaction and method of working up the reaction product amply justified the expectations, and a series of products apparently representing various grades of oxidation and directly giving green or violet colouration with sulphuric acid were obtained. A thorough study into these products, however, has been postponed for the present, owing to the fact that the attention of the author had to be first devoted to the study of the most interesting product of this reaction, which proved to be an isomer of conessine, and has therefore been named as iso-conessine.

When a solution of conessine in sulphuric acid was allowed to stand at room temperature (mean 40° C.) for 24 hours or heated for half an hour on the water-bath, no iso-conessine could be obtained from the reaction mixture, the basic products obtained thereby being bright yellow amorphous powders partly soluble and partly insoluble in water, the later fraction also indicating the presence of an acidic group in the molecule. When water was slowly added to a solution of conessine in sulphuric acid (conc.) immediately after its preparation at room temperature till the sequence of colours from reddish yellow to violet was completed, about 20% of iso-conessine was obtained through its sparingly soluble hydroiodide. When, on the other hand, conessine was carefully dissolved in concentrated sulphuric acid in the cold, the evolution of sulphur dioxide fumes otherwise copiously produced in the

[3] Polstorff, *Ber.*, 1886, **19**, 1682.
Ulrici, *Arch. Pharm.*, 1918, **256**, 57.
Giemsa and Halberkann, *Arch. Pharm.*, 1918, **256**, 201.

process being thus limited to a minimum and the well-cooled solution was slowly poured over a large quantity of pounded ice with constant and vigorous stirring, the yield of isoconessine increased to about 80%, the oxidation products forming only about 15 to 20% of the quantity of conessine taken.

Parallel studies with iso-conessimine and conimine gave similar results though the action of sulphuric acid was not so energetic as in the case of conessine, and from each of them the corresponding isomers could be isolated through the respective sparingly soluble hydroiodides without much difficulty.

None of these isomers, which form nearly colourless treacles and are readily soluble in all the usual organic solvents, could be so far induced to crystallise from any of them, but all their salts crystallise with especial readiness in well-defined characteristic forms. The uniformity of the bases was in each case tested through a process of fractional crystallisation of the hydroiodide and, in the case of iso-conessine, also with the help of fractional distillation and determination of the optical activity of the different fractions thereby obtained, the melting points and mixed melting points of the corresponding hydroiodides serving as a further check.

An interesting feature about the isomers of the conessine series is that their optical activity is about thrice as pronounced in the positive direction as in the case of the corresponding bases of the conessine series. Still more significant is the fact that, so far as could be judged from parallel experiments on the action of conessine and isoconessine on the respiration of frogs, the latter base is about thrice as potent as the former. This is a factor, indeed, which promises to place the therapeutic value of the Holarrhena alkaloids on quite a different plane, and carries the likelihood of iso-conessine eventually proving to be one of the most potent medicines in combating amœbic dysentery.

The experimental portion of the paper gives in each case only the best method worked out for obtaining the different isomers and does not include the details of studies in the action of sulphuric acid, which would be taken up in a subsequent communication on the oxidation products referred to above. The isomer of iso-conessimine, which has been named as iso-nor-iso-conessine[4] to avoid confusion in the nomenclature of the two mono-secondary bases of the conessine group, namely, conessimine and iso-conessimine, has been noted to form benzoyl and acetyl derivatives, but these are not described in the experimental part, as they could not so far be induced to crystallise or yield

[4] The name "nor-iso-conessine" has been reserved for the isomer of conessimine, which could not be studied for the present owing to lack of sufficient quantity of the base.

products pure enough for analysis. Its secondary character could, however, be satisfactorily fixed through the nitrogen and chlorine estimations of the crystalline hydrochloride of its nitroso derivative. Iso-conimine also yielded non-basic benzoyl, acetyl and nitroso derivatives, of which the two latter could be obtained pure enough to give fairly satisfactory analyses and have been described in the experimental part.

The iso-bases were found to contain the same number of N-methyls (determined in the hydroiodides) as the corresponding bases of the conessine series. The fixing up of a single double bond in iso-conessine presented special difficulty as on titration against bromine in chloroform solution a major portion of the base is converted into a crystalline product, which proved to be iso-conessine dihydrobromide, from which iso-conessine was liberated and identified. In glacial acetic acid solution also the major fraction of the base was obtained as dihydrobromide on treatment with 2 molecules of bromine, and the bromination product, formed thereby, could not be obtained in a characterisable condition. Ulrici (*loc. cit.*) noted that on liberation of the base from the bromination product of conessine only a mono-bromo derivative could be obtained, one bromine having been secondarily eliminated as HBr. The same thing apparently happens with greater readiness in the case of iso-conessine, the HBr eliminated from the initially formed addition product being taken up by the major portion of the unchanged base which is thrown out of solution as the hydro-bromic acid salt. The quantity of iso-conessine hydrobromide obtained in this case makes it even probable that the fresh double bond produced by the elimination of HBr preferentially adds on further bromine and HBr is subsequently eliminated till all the iso-conessine has been precipitated out as dihydrobromide. A single double bond in the iso-conessine series could, however, be conclusively established by titration of the non-basic diacetyl iso-conimine against bromine in chloroform solution in the cold whereby two atoms of bromine were used up yielding the brominated product as a cream-coloured crystalline powder.

The nature of the change introduced into the molecule of conessine through its isomerisation is not yet clear. From the facts stated above, however, it appears quite certain that concentrated sulphuric acid initially changes conessine into iso-conessine, which in turn is slowly oxidised. Comparative studies in the relationship between the chemical characteristics and pharmacological action of conessine and iso-conessine have also been taken up and some interesting results already obtained, which will be shortly communicated.

Experimental.

Action of concentrated sulphuric acid on conessine.—50 g. conessine were added in small portions to 150 c.c. H_2SO_4 (conc.) with efficient ice cooling and constant shaking. Complete solution was effected in about half an hour. The colour of the solution which was initially bright yellow changed into deep red and sulphur dioxide fumes were evolved in the process of solution. Before the colour began to darken the solution was very slowly added on to about 2 kg. of well-pounded ice in a large beaker with constant and vigorous stirring when a dirty yellow aqueous solution was obtained. On making the solution alkaline with NaOH the base was liberated as a straw-coloured, emulsive oily product which was shaken out with ether. From the ethereal solution the base was shaken out with dilute acetic acid and a concentrated aqueous solution of potassium iodide added till it was distinctly turbid. On cooling the hydroiodide immediately began to crystallise out, yielding 50 g. of nearly colourless hydroiodide (m.p. 322–23°) after a single crystallisation of the crude, crystalline precipitate from methanol. The combined mother liquors yielded after liberation of the base and a tedious process of purification 5 g. more of the above hydroiodide and about 10 g. of a slightly reddish treacle, which did not form a water or alcohol insoluble hydroiodide or oxalate, and therefore appeared to be free of both conessine and iso-conessine. From the combined alkaline aqueous layers, left after removal of the ether soluble base, about 5 g. of a flesh-coloured, ether insoluble, benzol and water-soluble powder were obtained on shaking out with chloroform. This as well as the reddish treacle, mentioned above, appear to form the products of oxidation of conessine and would be discussed in a subsequent paper.

The total hydroiodide obtained above (55 g.) was dissolved in 10% acetic acid (about 500 c.c.) in the hot, treated with charcoal and fractionally crystallised, whereby three successive fractions of 24 g., 17 g. and 6 g. were obtained, which melted between 324° and 25°, no depression in the melting point being perceptible on admixture of the first and the third fractions. The mother liquor which had got coloured in the process of concentration on the water-bath yielded after purification through the base and subsequent treatment with charcoal in acetic acid solution, about 4 g. more of the colourless hydroiodide melting at 325-26°.

Iso-conessine.

Iso-conessine, ($C_{24}H_{40}N_2$).—50 g. pure hydroiodide were dissolved in 10% acetic acid in the hot and the base liberated with caustic soda solution in the cold when it came out in white flocks which appeared to form a crystalline silky mass in the cold but turned buttery at room temperature. Taken up in ether, dried over sodium sulphate and freed of the solvent completely *in*

vacuo, iso-conessine was obtained as a light straw-coloured treacle which was easily soluble in all the usual organic solvents and failed to crystallise from any of them. It distils at 239–41°/3 mm. and in 1% absolute alcoholic solution showed $[\alpha]_D^{35°} = +97°$. On fractional distillation of 7 g. of the base into three equal fractions, each of them showed within limits of error the same optical activity. Further, the hydroiodide from each of the fractions showed the same melting point as the pure hydroiodide from which the base was liberated. In sulphuric acid (conc.) it directly dissolves to a bright yellow solution and on gradual addition of water gives the same sequence of colours as noted for conessine. [On macroanalysis after drying iso-conessine at 110° *in vacuo*, whereby partial volatilisation takes place, Found: C, 80·43; H, 11·59; N, 8·27; $C_{24}H_{40}N_2$ requires C, 80·89; H, 11·24; N, 7·87%.]

Iso-conessine hydroiodide, prepared as noted above and melting at 325–26° (decomp.), is very sparingly soluble in water and alcohol and crystallises out of these in aggregates of thin pentagonal plates (Plate XXI, Fig. 1) quite distinct from the conessine hydroiodide, which forms bunches and stars of stout prismatic rods melting at 308° (decomp.) (Plate XXI, Fig. 2). [After drying to constant weight at 100° *in vacuo* found: CH_3, 7·7; $C_{24}H_{40}N_2$ 2HI requires for (3 N–CH_3) CH_3, 7·35 %.]

Iso-conessine hydrochloride.—On adding ethereal HCl to the dry ethereal solution of the base, it came out as a white gelatinous mass which turned crystalline on rubbing. It is soluble in hot alcohol, less so in the cold and crystallises out of its hot concentrated solution on cooling in flat, silky, snow-white needles, which soften at 313° and melt at 318°(decomp.) [Conessine HCl browns at 335° and melts at 338–40° (decomp.)]. It is readily soluble in water and showed in 1% aqueous solution $[\alpha]_D^{36°} = +72°$ (Conessine HCl showed in 1% aqueous solution $[\alpha]_D^{35°} = +15·2°$). It crystallises from 96% alcohol with 2 molecules of water of crystallisation (Found: H_2O, 7·2; $C_{24}H_{40}N_2 2HCl·2H_2O$ requires H_2O, 7·7%.). After dehydration at 100° *in vacuo* (Found: Cl, 16·58; N, 6·19; $C_{24}H_{40}N_2·2HCl$ requires Cl, 16·55; N, 6·53%).

Iso-conessine chloroplatinate came out on addition of a 3% aqueous solution of platinic chloride to an aqueous solution of the hydrochloride as a cream-yellow crystalline mass. It is very difficultly soluble in hot alcohol and water and crystallises on concentration of its aqueous solution in clusters of needles which begin to darken at 250° and melt at 271–73° [Found: Pt, 25·44; $C_{24}H_{40}N_2H_2PtCl_6$ requires Pt, 25·47%].

Iso-conessine aurichloride.—On adding 5 % aqueous gold chloride solution to the aqueous solution of the hydrochloride in the cold, the gold salt was precipitated as a granular mass, which soon turned crystalline yielding bunches and stars of stout golden yellow needles and rods, sparingly soluble in alcohol

or water and melting at 293°-95° (decomp.) [Found : Au, 37·5; $C_{24}H_{40}N_2(HCl \cdot AuCl_3)_2$ requires Au, 38·0 %].

Iso-conessine picrate was prepared by adding aqueous picric acid to an aqueous solution of the hydrochloride. It is nearly insoluble in water, slightly soluble in hot alcohol out of which it crystallises in aggregates of prismatic plates and spear-shaped prismatic rods, which darken at 237° and melt at 240–42° (decomp.).

Iso-conessine hydrobromide was obtained on adding a concentrated solution of KBr to a concentrated aqueous solution of the hydrochloride when it separated out in aggregates of white slender needles, which when filtered, washed with very little water and dried on a porous plate *in vacuo*, formed a white powder, fairly soluble in alcohol and water, less so in water containing a little KBr. Crystallised from a litttle hot alcohol it darkens at 315° and melts at 318–22° (decomp.).

The oxalate came out as an oil on bringing together the components in acetone solution, and on washing with acetone and drying *in vacuo* over phosphorous pentoxide, it formed a cream-coloured amorphous hygroscopic powder which in sharp contrast to conessine oxalate was exceedingly soluble in alcohol and water and failed to crystallise from any of the solvents.

Iso-conessine dimethoiodide.—On adding 3·2 g. methyl iodide (4 mols.) to a solution of 2 g. base (1 mol.) in 25 c.c. acetone and keeping the reaction mixture at room temperature (40°), the methoiodide soon began to separate in shining silky plates. The reaction, however, appeared to be much slower than in the case of conessine as was observed in a parallel experiment. On working up the product after keeping the mixture well corked overnight, the methoiodide was obtained in nearly theoretical yield. Recrystallised from hot alcohol, in which it is sparingly soluble, it formed a colourless crystalline powder insoluble in acetone or other organic solvents, difficultly soluble in water and melting at 316–18° (decomp.) [Found : I, 40·01 ; CH_3, 12·38; $C_{24}H_{40}N_2(CH_3I)_2$ requires I, 39·7 ; (for 5 N–CH_3) CH_3, 12·11 %).

Addition of bromine.—1·0156 g. isoconessine in 5 c.c. $CHCl_3$ was titrated against bromine in chloroform solution with ice cooling. Following the titration with potassium iodide starch paper it took 0·5092 g. bromine as against 0·4565 g. required for 1 double bond. The white crystalline product which separated out in the course of titration when washed with ether and dried, formed 1·02 g. The filtrate gave a little more of the same product on addition of ether and petroleum ether. On removal of the solvent from the final filtrate by slow evaporation exposed to air, a coloured oily product was obtained, which contained bromine, was readily soluble in all the organic

solvents, quickly darkened and could not be analysed. The crystalline product obtained above showed the same melting point as iso-conessine dihydrobromide (318–22° decomp.), and gave no depression in its melting point on admixture with it.[5] On liberation of the base it gave iso-conessine which was identified through its hydroiodide. Analysed directly it gave too high values of bromine due apparently to the tendency of the hydrobromide to form an unstable addition compound with bromine, but after heating to constant weight at 140° it gave the required value [Found : Br, 30·51 ; $C_{24}H_{40}N_2 2HBr$ requires Br, 30·88%].

In a subsequent experiment 0·9 g. iso-conessine was dissolved in 5 c.c. glacial acetic acid and 0·4045 g. bromine (required for 1 double bond) in glacial acetic acid (5 c.c.) was slowly added to the solution with cooling. There was decolourisation first but the solution got coloured on addition of the whole quantity. After standing for about an hour a voluminous white crystalline precipitate came out, which was filtered after keeping for an hour longer, washed with glacial acetic acid and finally with a large quantity of ether. The product thus obtained was identified as iso-conessine dihydrobromide through its melting point and mixed melting point. The base from the combined filtrates was nearly colourless in ethereal solution in the beginning and on quick evaporation under the fan was obtained as a straw-coloured oily residue, which was readily soluble in all the usual organic solvents, failed to crystallise from any of them, soon developed a red colour darkening on further keeping and was rich in halogen (flame test).

Action of Sulphuric Acid on Iso-Conessimine.

10 g. iso-conessimine were added in small portions to 100 c.c. sulphuric acid (conc.) with ice water cooling in the beginning and later on at room temperature with vigorous shaking. The solution was completed in about 20 minutes time during which the colour changed from lemon yellow to golden yellow, orange and finally orange red. At this stage the solution was added on to about 500 g. of well-pounded ice with constant stirring. On liberating the base from the pale greenish-yellow solution in the cold and repeatedly shaking it out with ether, about 8·5 g. of a yellowish treacle were obtained. This was dissolved in acetic acid and treated with potassium iodide solution in the cold whereby a crystalline hydroiodide (11 g.) and from its filtrate about 1 g. of base which did not form any insoluble hydroiodide were finally obtained.

[5] In respect of the melting points of high melting salts (above 300°) of both conessine and iso-conessine series, it may be noted that they largely vary within a range of about 10° according to the rate of heating, and all the comparative melting points and mixed melting points noted in the paper are based on parallel observations.

The hydroiodide was fairly soluble in water when freshly precipitated but in the process of recrystallisation it gradually became very insoluble in water particularly after drying in the air. Its solubility in ethyl and methyl alcohol also decreased in the same proportion. The pure hydroiodide, as obtained on washing the crude product with acetone and crystallising it out of water after treating the aqueous solution with charcoal in the hot, melted at 289°, two subsequent crops melting at 288° and 285–87° respectively. The melting point of iso-conessimine hydroiodide as already reported by the author and observed in a freshly prepared sample is 316°.

Iso-Nor-Iso-Conessine.

Iso-nor-iso-conessine, $C_{23}H_{38}N_2$.—10 g. of the pure hydroiodide obtained above were dissolved in hot water and the base liberated with caustic soda solution and shaken out with ether. On drying the ethereal solution and removing the solvent finally *in vacuo* at 100°, 6·5 g. iso-nor-iso-conessine were obtained as a straw-coloured treacle, which was easily soluble in all the usual organic solvents and could not so far be crystallised from any of them. In 1% absolute alcoholic solution it showed $[\alpha]_D^{35°} = +101°$ as against $+30°$ noted for iso-conessimine. [After drying *in vacuo* at 110° found: C, 80·20; H, 11·38; N, 7·94; $C_{23}H_{38}N_2$ requires C, 80·70; H, 11·11; N, 8·20%.]

——*hydroiodide*, prepared as noted above (m.p. 289° decomp.)is sparingly soluble in alcohol and water and crystallised out of these in aggregates of white silky rods and plates (Plate XXI, Fig. 3). [Found: CH_3, 5·08; $C_{23}H_{38}N_2 2HI$ requires (for 2 N–CH_3) CH_3, 5·02%.]

——*hydrochloride*, prepared from the components in ethereal solution, is exceedingly soluble in water and alcohol and insoluble in other organic solvents and crystallises from a mixture of alcohol and acetone in white glistening rectangular plates, melting at 335° (decomp.), its mixed melting point with iso-conessimine hydrochloride (which crystallised from the same solvents in prismatic rods also melting at 335°) being 318–20°. In 1% aqueous solution it showed $[\alpha]_D^{35°} = +72·80°$ as against $+7·5°$ noted in a parallel observation for iso-conessimine hydrochloride. [Found: Cl, 16·7; $C_{23}H_{38}N_2 2HCl$ requires 17·1%.]

——*picrate*, prepared by adding aqueous picric acid to a solution of the base in dilute hydrochloric acid, is sparingly soluble in cold, fairly so in hot water and crystallises from it on cooling in aggregates of tapering prismatic rods. It is also fairly soluble in hot methanol and crystallises out of it on slow concentration in conical prisms, which began to shrink at 143° and slowly melted down giving a meniscus at 166°.

Iso-conessimine picrate crystallises from hot methanol in rectangular plates melting with decomposition at 198–200°.

——*chloro-platinate* came out on adding aqueous platinic chloride to an aqueous solution of the hydrochloride in clusters of short tapering light orange-coloured needles, which darkened at 284° and melted at 290–92° (decomp.) [Found : Pt, 25·95 ; $C_{23}H_{38}N_2 2HCl \cdot PtCl_4$ requires Pt. 25·90%].

Methylation of iso-nor-iso-conessine : iso-conessine.—Attempts to methylate the secondary to the tertiary bases were as unsuccessful in the iso-series as in the case of the secondary bases of the conessine series. Thus methyl iodide and iso-nor-iso-conessine in ethereal solution gave an undefinable crystalline product melting within a wide range of 280–300°. When the base, however, was refluxed on the water-bath for about an hour with 1·5 mols. each of formic acid and formaldehyde and diluted with water it gave a clear light yellow solution which, on treating with a solution of potassium iodide, gave pure iso-conessine hydroiodide, which showed no depression in its melting point on admixture with pure iso-conessine hydroiodide and yielded a base showing the same optical activity as iso-conessine (yield about 80%).

Nitroso-iso-nor-iso-conessine.—To a solution of the base (1 g.) in normal HCl was added in the cold a concentrated solution of sodium nitrite till strongly turbid. After keeping for some time in the cold, a yellowish oil separated out which turned crystalline on cooling and rubbing. The crystalline nitroso-hydrochloride thus obtained was macerated with NaOH and extracted with ether. The ethereal solution when washed with water and dried over sodium sulphate gave on removal of the solvent the nitroso base as a straw-coloured treacle, which was insoluble in water, soluble in ether, petroleum ether and other organic solvents and failed to crystallise from any of them.

——*hydrochloride*, prepared from the components in ethereal solution, forms aggregates of colourless stout prismatic rods. It is difficultly soluble in 10% HCl, easily in water and alcohol, shrinks at 274° and melts at 282–84°. [After drying to constant weight at 100° *in vacuo* found : N, 9·48 ; Cl, 8·97 ; $C_{23}H_{37}N_2NO \cdot HCl$ requires N, 10·30 ; Cl. 8·58%.]

Action of Sulphuric Acid (Conc.) on Conimine.

5 g. conimine added on to 25 c.c. sulphuric acid (conc.) with constant stirring and initial cooling gave a deep red solution, which, when worked up as in the case of iso-conessimine, yielded 5 g. of pure recrystallised hydroiodide melting at 332°, about 0·6 g. of an ether soluble base which did not form an insoluble hydroiodide and a little quantity of ether insoluble water soluble base which could be shaken out with chloroform from the alkaline aqueous

cooling till strongly turbid. A white sticky mass separated which was taken up in ether. The ethereal solution, successively washed with dilute HCl, alkali and then water, yielded on drying and removing the solvent a straw-coloured treacle which turned into a crystalline powder on rubbing with ether and a little petroleum ether. On slow evaporation of its solution in acetone in which it was exceedingly soluble, it forms broom-like aggregates of long tapering needles. It is easily soluble in alcohol, insoluble in water and crystallised from a mixture of alcohol and water in aggregates of short stout prismatic rods which shrink at 120° and melt at 123–25° [Found: N, 13·33 ; $C_{22}H_{34}N_2(NO)_2$ requires N, 14·50%].

Diacetyl iso-conimine.—0·5 g. iso-conimine with 1 g. each of acetic anhydride and anhydrous sodium acetate was heated in the water-bath for 3 hours and diluted with water. The nearly colourless oil which remained undissolved was taken up in ethyl-acetate, which was successively washed with dilute hydrochloric acid, alkali and finally water. On drying and concentrating the ethyl-acetate solution, the diacetyl compound was obtained as a nearly white crystalline powder (0·4 g.) which was easily soluble in alcohol and acetone, difficultly in ether and petroleum ether, insoluble in water and dilute acids or alkalies and melted at 190–91° after shrinking at 185°. The m.p. of diacetyl conimine was 139–40°. [Found: C, 74·83 ; H, 9·48 ; $C_{22}H_{34}N_2(CO\cdot CH_3)_2$ requires C, 75·72 ; H, 9·71%.]

Di-methyl-iso-conimine : *Iso-conessine.*—A solution of 0·5 g. of the base in the least quantity of formic acid was refluxed with 2·5 mols. of formaldehyde for an hour. The reaction mixture was light straw-coloured as against deep red to reddish brown in the case of similar methylations in the conessine series. The base obtained from it was identified as iso-conessine through its optical activity and the melting point of the hydroiodide.

Bromination of diacetyl conimine.—0·1186 g. diacetyl conimine in 3 c.c. chloroform titrated against bromine in chloroform solution with ice cooling and constant stirring, took up 0·048 g. bromine as followed by potassium iodide starch paper (required for 1 double bond 0·046 g.). On approaching the saturation point the solution began to grow slightly turbid. On adding dry ether and petroleum ether to the resultant pale-yellow chloroform solution a cream-coloured crystalline, hygroscopic powder was obtained which was insoluble in water, soluble in alcohol and acetone, nearly insoluble in ether and petroleum ether, began to shrink at 177° and melted with frothing at 185–86°.

STUDIES IN THE CHEMISTRY OF CHALCONES AND CHALCONE-OXIDES.

I. Phenyl-(3'4-Methylene-dioxy-styryl)-ketone.

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THE marked reactivity of chalcones and chalcone-oxides makes it of interest to examine how far this reactivity is affected by the presence of other groups in the nuclei. A comparative study has now been made of the reactivities of phenyl-(3·4-methylene-dioxy-styryl)-ketone (I ; $R_1 = CH_2O_2C_6H_3-$) which contains an electron source (methylene-dioxy-group) and of phenyl-(3·4-methylene-dioxy-6-nitro-styryl)-ketone (I ; $R_1 = CH_2O_2C_6H_2NO_2-$) which contains an electron sink (nitro group) in addition to the electron source.

$R_1 = CH_2O_2C_6H_3-$ or $CH_2O_2C_6H_2NO_2-$ or C_6H_5-
$R_2 = CH_2O_2C_6H_2 =$. $R' = CH_3$ or C_2H_5.

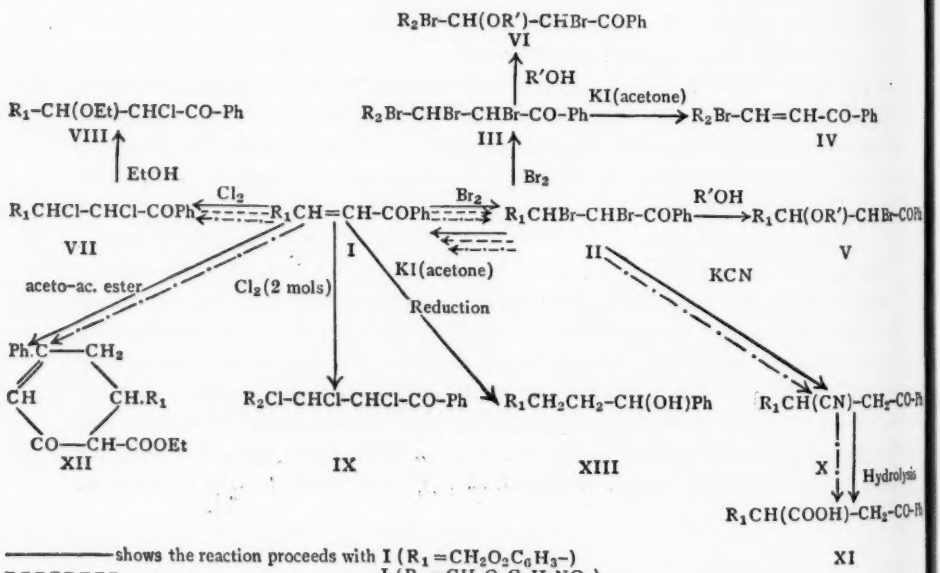

FIG. 1.

Phenyl-(3·4-methylene-dioxy-styryl)-ketone (I ; $R_1 = CH_2O_2C_6H_3-$; see Fig. 1) with bromine (1 mol.) yielded α-benzoyl-β-(3·4-methylene-dioxy-phenyl)-α-β-dibromo-ethane (II ; $R_1 = CH_2O_2C_6H_3-$)[1] which with boiling ethyl or methyl alcohol gave respectively *α-benzoyl-α-bromo-β-ethoxy-β-(3·4-methylene-dioxy-phenyl)-ethane* (V ; R′=Et) and *α-benzoyl-α-bromo-β-methoxy-β-(3·4-methylene-dioxy-phenyl)-ethane* (V ; R′=Me). The labile nature of one of the bromine atoms in compounds of the type (II) has been already observed by Pond and Shoffstall[2] with α-benzoyl-β-(*p*-methoxy-phenyl)-α-β-dibromo-ethane (II ; $R_1 = CH_3O-C_6H_4-$)which contains a methoxy-group in the nucleus. These authors assumed that the bromine atom in the α-position to the keto-group was replaced by the alkyl group, because the elimination of alcohol by heating the alkoxy-compound (V ; $R_1 = CH_3O-C_6H_4-$, R′=Me) gave a mono-bromo-anisylidene-acetophenone identical with the compound obtained by the action of sodium ethoxide on the dibromo-compound (II ; $R_1 = CH_3O-C_6H_4-$). Following Wislicenus,[3] they supposed that this bromine was in the β-position to the keto-group. Dufraisse and his collaborators,[4] however, have shown that the bromine in mono-bromo-chalcones obtained by the action of sodium alcoholate on the chalcone dibromides of the type (II) is in the α-position and hence the formula now given to (V) is to be preferred. Further support is given to the formula now adopted by the consideration that the nucleus containing the activating group may be expected to influence the nearer bromine atom.*

(I ; $R_1 = CH_2O_2C_6H_3-$) with bromine (2 mols.) gave *α-benzoyl-β-(3·4-methylene-dioxy-6-bromo-phenyl)-α-β-dibromo-ethane* (III ; $R_2 = CH_2O_2C_6H_2=$) which with the corresponding alcohols yielded respectively *α-benzoyl-α-bromo-β-ethoxy-β-(3·4-methylene-dioxy-6-bromo-phenyl)-ethane* (VI ; R′=Et) and *α-benzoyl-α-bromo-β-methoxy-β-(3·4-methylene-dioxy-6-bromo-phenyl)-ethane* (VI ; R′=Me). Heated with potassium iodide (2 mols.) in acetone both (II) and (III ; $R_2 = CH_2O_2C_6H_2=$) reformed the corresponding chalcones (I) and (IV ; $R_2 = CH_2O_2C_6H_2=$). The constitution of (IV) as *phenyl-(3·4-methylene-dioxy-6-bromo-styryl)-ketone* and hence of (III) is proved by the synthesis of (IV ;

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[1] Bauer and Werner, *Ber.*, 1922, **55**, 2497.

[2] *J.A.C.S.*, 1900, **22**, 658 ; *cf.* Werner, *Ber.*, 1906, **39**, 35, who describes Pond and Shoffstall's compounds without reference to their work, and assumes that the bromine atom in the β-position to the keto-group is replaced ; see also Goldschmiedt, 1906, **39**, 651 ; Bauer and Vogel, *J.pr.Chem.*, 1913, **88**, 329 ; Angeli, *Atti R.Acad.Lincei*, 1924, (v), **33**, 109 ; for similar work on alkoxycinnamic acid dibromides see Hoering, *Ber.*, 1907, **40**, 2174.

[3] *Ann.*, 1899, **308**, 219.

[4] *Compt. rend.*, 1920, **171**, 1062 ; 1921, **173**, 985 ; 1922, **174**, 1631.

* Motwani in this laboratory has recently shown that a methoxy-group in the other nucleus does not enhance the reactivity of the bromine atoms.

$R_2 = CH_2O_2C_6H_2 =$), from 6-bromo-piperonal and acetophenone. (I) with chlorine (1 mol. and 2 mols.) formed respectively, α-benzoyl-β-(3·4-methylene-dioxy-phenyl)-α-β-dichloro-ethane (VII) and *α-benzoyl-β-(3·4-methylene-dioxy-6-chloro-phenyl)-α-β-dichloro-ethane* (IX ; $R_2 = CH_2O_2C_6H_2 =$). The constitution of (IX) was deduced by analogy with (III). (VII) which was isolated only in the form of paste yielded with ethyl alcohol, *α-benzoyl-α-chloro-β-ethoxy-β-(3·4-methylene-dioxy-phenyl)-ethane* (VIII).

The dibromide (II ; $R_1 = CH_2O_2C_6H_3 -$) with potassium cyanide gave *α-(3·4-methylene-dioxy-phenyl)-β-benzoyl-propio-nitrile* (X ; $R_1 = CH_2O_2C_6H_3 -$) which on hydrolysis formed *α-(3·4-methylene-dioxy-phenyl)-β-benzoyl-propionic acid* (XI ; $R_1 = CH_2O_2C_6H_3 -$). The formulæ of (X) and (XI) were confirmed by the fact that benzylidene-acetophenone-dibromide (II ; $R_1 = C_6H_5 -$) with potassium cyanide gave α-phenyl-β-benzoyl-propio-nitrile (X ; $R_1 = C_6H_5 -$) which has been synthesised previously from phenyl-styryl-ketone and hydrogen cyanide by Hann and Lapworth.[5] This nitrile on hydrolysis gave α-phenyl-β-benzoyl-propionic acid (XI ; $R_1 = C_6H_5 -$) which has also been previously prepared.[6]

Phenyl-(3·4-methylene-dioxy-6-nitro-styryl)-ketone (I ; $R_1 = CH_2O_2 : C_6H_2NO_2 -$) with bromine (1 mol.) gave *α-benzoyl-β-(3·4-methylene-dioxy-6-nitro-phenyl)-α-β-dibromo-ethane* (II ; $R_1 = CH_2O_2C_6H_2NO_2 -$), which did not react further with bromine or with alcohol but was converted into (I ; $R_1 = CH_2O_2C_6H_2NO_2 -$) by the action of potassium iodide in acetone. By the action of chlorine (1 mol.) on (I ; $R_1 = CH_2O_2C_6H_2NO_2 -$), *α-benzoyl-β-(3·4-methylene-dioxy-6-nitro-phenyl)-α-β-dichloro-ethane* (VII; $R_1 = CH_2O_2C_6H_2NO_2 -$) was obtained.

(I ; $R_1 = CH_2O_2C_6H_3 -$) condensed readily with ethyl-aceto-acetate to yield *ethyl-2-(3′·4′-methylene-dioxy-phenyl)-4-phenyl-* Δ ^{4}*-cyclohexene-6-one-1-carboxylate* (XII ; $R_1 = CH_2O_2C_6H_3 -$).[7] The nitrochalcone (I ; $R_1 = CH_2O_2C_6H_2NO_2 -$) did not react. (I ; $R_1 = CH_2O_2C_6H_3 -$) was reduced by hydrogen in presence of palladium, to give *α-phenyl-γ-(3·4-methylene-dioxy-phenyl)-propylalcohol* (XIII ; $R_1 = CH_2O_2C_6H_3 -$) (m.p. 95–96°). The saturated ketone, *i.e.*, dihydropiperonal-acetophenone (m.p. 39–40°)[8] was not obtained. The nitrochalcone (I ; $R_1 = CH_2O_2C_6H_2NO_2 -$) could not be reduced.

(I ; $R_1 = CH_2O_2C_6H_3 -$; see Fig. 2) with hydrazine hydrate gave *3-phenyl-5-(3′·4′-methylene-dioxy-phenyl)-pyrazoline* (XIV ; $R_1 = CH_2O_2C_6H_3$-)

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[5] *J.C.S.*, 1904, **85**, 1359.

[6] Hann and Lapworth, *loc. cit.*

[7] Knœvenagel, *Ann.*, 1894, **281**, 58 ; see also Dieckmann and Fischer, *Ber.*, 1911, **44**, 969.

[8] Bargellini and Bini, *Gazetta*, 1911, **41**, II, 435.

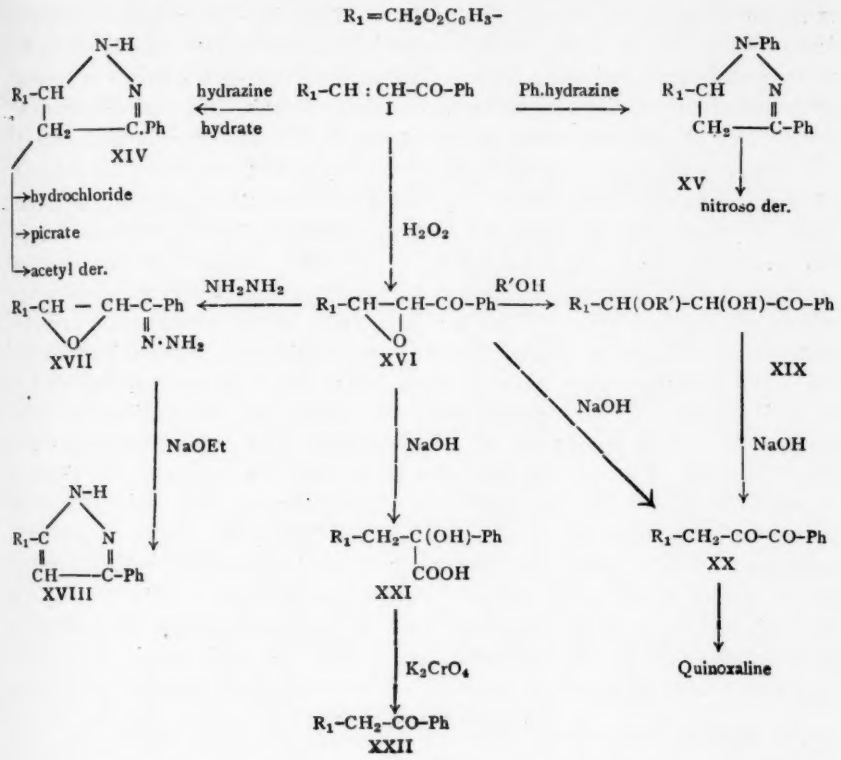

FIG. 2.

which was unstable, but formed a stable *hydrochloride*, *picrate* and *acetyl-derivative*. The substance did not give Knorr's pyrazoline colour reaction, *i.e.*, a trace dissolved in conc. sulphuric acid gave no colour with a drop of ferric chloride or sodium nitrite solution. This points to it being a hydrazone.[9] On the other hand unlike hydrazones, it gave no ammonia on reduction with sodium amalgam, and formed a hydrochloride. The evidence is conflicting; as it seemed definitely basic, the more probable assumption is that it is a pyrazoline.

With phenyl-hydrazine (I; $R_1=CH_2O_2C_6H_3-$) gave 1-3-*diphenyl*-5-(3'·4'-*methylene-dioxy-phenyl*)-*pyrazoline* (XV; $R_1=CH_2O_2C_6H_3-$) which answered Knorr's pyrazoline's tests and gave a nitroso-derivative. With hydrogen peroxide (6%) (I; $R_1=CH_2O_2C_6H_3-$) gave the *oxide of phenyl*-(3·4-

[9] See Auwers and Voss, *Ber.*, 1909, **42**, 4417.

methylene-dioxy-styryl)-ketone (XVI ; $R_1 = CH_2O_2C_6H_3-$)[10] which yielded a *hydrazone* (XVII ; $R_1 = CH_2O_2C_6H_3-$) with hydrazine hydrate. (XVII) is taken to be a hydrazone and not a hydroxy-pyrazoline,[11] because it does not form a nitroso-derivative. With sodium ethylate or acetic anhydride, (XVII) gave 3-*phenyl*-5-(3′·4′-*methylene-dioxy-phenyl*)-*pyrazole* (XVIII ; $R_1 = CH_2O_2C_6H_3-$).

When a suspension of the oxide (XVI ; $R_1 = CH_2O_2C_6H_3-$) in methyl alcohol was treated with a little conc. sulphuric acid, the oxide ring ruptured with the formation of *α-benzoyl-α-hydroxy-β-methoxy-β-*(3·4-*methylene-dioxy-phenyl*)-*ethane* (XIX ; $R_1 = CH_2O_2C_6H_3-$; R′=Me). Ethyl alcohol reacted similarly giving *α-benzoyl-α-hydroxy-β-ethoxy-β-*(3·4-*methylene-dioxy-phenyl*)-*ethane* (XIX ; R′=Et). (XIX ; R′=Me) when boiled with sodium acetate and acetic acid, for two hours, or with aqueous-alcoholic sodium hydroxide for a few minutes, gave *phenyl-*(3·4-*methylene-dioxy-benzyl*)-*diketone* (XX ; $R_1 = CH_2O_2C_6H_3-$), the constitution of which as an α-diketone was confirmed by the formation of a *quinoxaline* with σ-phenylene-diamine. The formation of the α-diketone also establishes the structure of (XIX ; $R_1 = CH_2O_2C_6H_3-$; R′=Me and Et). The diketone was also obtained by boiling an alcoholic solution of (XVI ; $R_1 = CH_2O_2C_6H_3-$) with aq. sodium hydroxide for 30 seconds. The diketone gave a colour reaction with alcoholic ferric chloride showing that the enol form is present in the solution. (XVI ; $R_1 = CH_2O_2C_6H_3-$) on prolonged heating with sodium hydroxide gave *phenyl-*(3·4-*methylene-dioxy-benzyl*)-*glycollic acid* (XXI ; $R_1 = CH_2O_2C_6H_3-$). This acid was readily oxidised by potassium dichromate in acetic acid to *phenyl-*

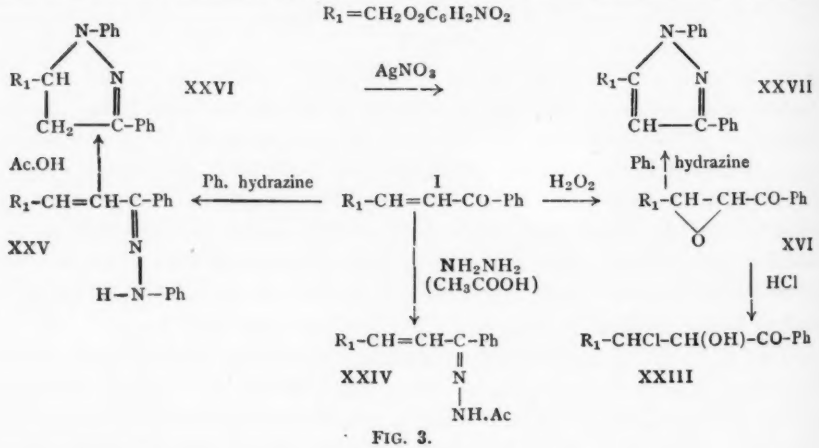

FIG. 3.

[10] See Baker and Robinson, *J.C.S.*, **1932**, 1798.

[11] See Widman, *Ber.*, **1916**, **49**, 2781.

(3·4-*methylene-dioxy-benzyl*)-*ketone* (XXII; $R_1=CH_2O_2C_6H_3-$) which has been previously prepared by Tiffeneau and Lévy[12] by the distillation of the oxide of (3·4-methylene-dioxy-styryl)-benzene. This oxidation proves the structure of the acid (XXI). (XVI; $R_1=CH_2O_2C_6H_3-$) did not give a definite product with HCl.

(I; $R_1=CH_2O_2C_6NO_2-$; see Fig. 3) with hydrogen peroxide (6%) gave the *oxide of phenyl*-(3·4-*methylene-dioxy*-6-*nitro-styryl*)-*ketone* (XVI; $R_1=CH_2O_2C_6H_3NO_2-$) which, however, was better prepared (quantitative yield) by the method of Widman and Almström[13] from 6-nitro piperonal and ω-bromo-acetophenone. (XVI; $R_1=CH_2O_2C_6H_2NO_2-$) unlike (XVI; $R_1=CH_2O_2C_6H_3-$) did not react with ethyl or methyl alcohols or with NaOH, but with hydrogen chloride in acetic acid gave *phenyl-β-chloro-α-hydroxy-β*-(3·4-*methylene-dioxy*-6-*nitro-phenyl*)-*ethyl-ketone* (XXIII; $R_1=CH_2O_2C_6H_3NO_2-$), in which the position of chlorine atom was determined by the results of Widman.[14] (I; $R_1=CH_2O_2C_6H_2NO_2-$) with hydrazine hydrate in acetic acid gave the *acetyl derivative of the hydrazone of phenyl*-(3·4-*methylene-dioxy*-6-*nitro-styryl*)-*ketone* (XXIV; $R_1=CH_2O_2C_6H_2NO_2-$). Analysis of the product showed that it was an acetyl derivative of the hydrazone or pyrazoline. It is difficult to decide in this case between the alternative formulæ, since the acetyl group may mask the various tests. Auwers and Voss,[15] however, have shown that the nitro-group stabilises the hydrazone form and it has been found (see later) that the phenyl-hydrazone of the chalcone now under discussion is stable.

(I; $R_1=CH_2O_2C_6H_2NO_2-$) with phenyl-hydrazine in hot acetic acid gave the *phenyl-hydrazone of phenyl*-(3·4-*methylene-dioxy*-6-*nitro-styryl*)-*ketone* (XXV; $R_1=CH_2O_2C_6H_2NO_2-$) which did not give Knorr's pyrazoline colour reaction and dissolved slowly in conc. sulphuric acid with the formation of colour. When boiled with acetic acid, it yielded 1·3-*diphenyl*-5-(3′·4′-*methylene-dioxy*-6′-*nitro-phenyl*)-*pyrazoline* (XXVI; $R_1=CH_2O_2C_6H_2NO_2-$) which answered the pyrazoline colour tests. (XXVI) was converted by silver nitrate into 1·3-*diphenyl*-5-(3′·4′-*methylene-dioxy*-6′-*nitro-phenyl*)-*pyrazole* (XXVII; $R_1=CH_2O_2C_6H_2NO_2-$) which was also obtained by the action of phenyl-hydrazine on (XVI; $R_1=CH_2O_2C_6H_2NO_2-$).

A study of the experimental results indicates that the nitro-group removes the enhanced activity which the presence of a nuclear alkoxy group

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[12] *Compt. rend.*, 1930, **190**, 1510.

[13] *Ann.*, 1913, **400**, 105.

[14] *Ber.*, 1916, **49**, 477; *cf.* Jörlander, *Ber.*, 1916, **49**, 2783; 1917, **50**, 1457; Bodforss, *Ber.*, 1916, **4**', 2795, and Baker and Robinson, *loc. cit.*

[15] *Ber.*, 1909, **42**, 4414.

confers on one of the bromine atoms in the chalcone dibromide ; and further it reduces the reactivity of the oxide towards ethyl or methyl alcohols and alkali, but not towards HCl.

Experimental.

1. *α-Benzoyl-β-(3·4-methylene-dioxy-phenyl)-α-β-dibromo-ethane* (II ; $R_1 = CH_2O_2C_6H_3-$) was prepared by the action of bromine (1 mol.) on (I ; $R_1 = CH_2O_2C_6H_3-$).[16] (Found : Br, 39·0 ; $C_{16}H_{12}O_3Br_2$ requires Br, 38·8%).

2. *α-Benzoyl-α-bromo-β-ethoxy-β-(3·4-methylene-dioxy-phenyl)-ethane* (V ; $R_1 = CH_2O_2C_6H_3-$; $R' = Et$).—The preceding dibromide was boiled with ethyl alcohol for fifteen minutes ; on cooling the solution, white prisms separated, m.p. 143–44°. (Found : Br, 21·1 ; $C_{18}H_{17}O_4Br$ requires Br, 21·2%).

3. *α-Benzoyl-α-bromo-β-methoxy-β-(3·4-methylene-dioxy-phenyl)-ethane* (V ; $R_1 = CH_2O_2C_6H_3-$; $R' = Me$).—Prepared as in (2) ; crystallised from methyl alcohol in prismatic needles m.p. 115–16°. (Found : Br, 22·1 ; $C_{17}H_{15}O_4Br$ requires Br, 22·0%).

4. *α-Benzoyl-β-(3·4-methylene-dioxy-6-bromo-phenyl)-α-β-dibromo-ethane* (III ; $R_2 = CH_2O_2C_6H_2=$).—Bromine (32 g.) in gl. acetic acid (50 c.c.) was added slowly to (I ; $R_1 = CH_2O_2C_6H_3-$) (25 g.) in hot acetic acid (150 c.c.), and the mixture was heated at 100° for 30 minutes, when (III ; $R_2 = CH_2O_2C_6H_2$:) separated in the form of crystalline needles (yield, 30 g.). It recrystallised from benzene-petroleum ether in white needles. m.p. 174–75°. (Found : Br, 49·3 ; $C_{16}H_{11}O_3Br_3$ requires Br, 48·9%). It formed (IV ; $R_2 = CH_2O_2C_6H_2=$) when treated with potassium iodide as described in (7).

5. *α-Benzoyl-α-bromo-β-ethoxy-β-(3·4-methylene-dioxy-6-bromo-phenyl)-ethane* (VI ; $R_2 = CH_2O_2C_6H_2=$; $R' = Et$) was prepared as in (2) ; it crystallised from ethyl alcohol in white needles, m.p. 126–27°. (Found : Br, 34·8 ; $C_{18}H_{16}O_4Br_2$ requires Br, 35·1%).

6. *α-Benzoyl-α-bromo-β-methoxy-β-(3·4-methylene-dioxy-6-bromo-phenyl)-ethane* (VI ; $R_2 = CH_2O_2C_6H_2=$; $R' = Me$) was prepared as in (2) ; it recrystallised from methyl alcohol in colourless prisms, m.p. 131–32°. (Found : Br, 36·3 ; $C_{17}H_{14}O_4Br_2$ requires Br, 36·2%).

7. *Phenyl-(3·4-methylene-dioxy-6-bromo-styryl)-ketone* (IV ; $R_2 = CH_2O_2C_6H_2$:).—(III ; $R_2 = CH_2O_2C_6H_2=$) (6 g.) in hot acetone was heated at 90–100° with potassium iodide dissolved in a small quantity of water and acetone, when iodine was liberated. The product separating on cooling recrystallised from alcohol-acetone in white needles, m.p. 146–47°. The substance turns pink on exposure for a few days. (Found : Br, 24·3 ; $C_{16}H_{11}O_3Br$ requires

[16] *cf.* Bauer and Werner, *loc. cit.*

Br, 24·2%). It was also formed when a mixture of 6-bromo piperonal (4·6 g.), alcohol (100 c.c.), acetophenone (2·4 g.) and sodium hydroxide solution (10% 2 c.c.) was heated at 80–100° for 15 minutes.

8. *α-Benzoyl-α-chloro-β-ethoxy-β-(3·4-methylene-dioxy-phenyl)-ethane* (VIII; $R_1=CH_2O_2C_6H_3-$).—An attempt to prepare a dichloro-compound (VII; $R_1=CH_2O_2C_6H_3-$) similar to (II; $R_1=CH_2O_2C_6H_3-$) by passing dry chlorine (1 mol.) into an acetic acid solution of (I; $R_1=CH_2O_2C_6H_3-$) (1 mol.) resulted in a pasty mass which could not be re-crystallised from any of the usual inert solvents. It recrystallised from ethyl alcohol (charcoal) in prismatic needles, m.p. 118–19°. (Found: Cl, 10·8; $C_{18}H_{17}O_4Cl$ requires Cl, 10·7%). Methyl alcohol did not give a crystalline product.

9. *α-Benzoyl-β-(3·4-methylene-dioxy-6-chloro-phenyl)-α-β-dichloro-ethane* (IX; $R_2=CH_2O_2C_6H_2=$).—An acetic acid solution of (I; $R_1=CH_2O_2C_6H_3-$) was treated with chlorine and kept over-night, when crystals separated; a further yield was obtained on dilution with water. The product recrystallised from benzene-petroleum ether in colourless crystals, m.p. 127–28°. (Found: Cl, 29·3; $C_{16}H_{11}O_3Cl_3$ requires Cl, 29·7%).

10. *α-(3·4-Methylene-dioxy-phenyl)-β-benzoyl-propio-nitrile* (X; $R_1=CH_2O_2C_6H_3-$).—A mixture of (II; $R_1=CH_2O_2C_6H_3-$) (20 g.), potassium cyanide (10 g.) and alcohol (100 c.c. methyl or ethyl) was heated under reflux for three hours at 100°, and kept at 0° for 24 hours, when the precipitate formed was filtered and washed with water and with alcohol (yield, 8 g.). It recrystallised from alcohol (charcoal) in white plates, m.p. 132–33°. (Found:* N, 5·1; $C_{17}H_{13}O_3N$ requires N, 5·0%).

11. *α-(3·4-Methylene-dioxy-phenyl)-β-benzoyl-propionic acid* (XI; $R_1=CH_2O_2C_6H_3-$).—A mixture of the preceding nitrile (5 g.) aq. sodium hydroxide (10%; 50 c.c.) and alcohol (25 c.c.) was heated at 100° for 8 hours and filtered. The filtrate was acidified with dil. hydrochloric acid and the acid (4·2 g.) separating was recrystallised from benzene; prismatic crystals m.p. 143–44°. (Found:† C, 68·7; H, 4·6; equiv. 294; $C_{17}H_{14}O_5$ requires C, 68·5; H, 4·7%; equiv. 298).

12. *α-Phenyl-β-benzoyl-propio-nitrile* (X; $R_1=C_6H_5-$).—α-Benzoyl-β-phenyl-α-β-dibromo-ethane (II; $R_1=C_6H_5$) treated as in (10) gave (X; $R_1=C_6H_5-$) m.p. 126–27°. (Found:*† N, 6·1; C, 81·7; H, 5·5; $C_{16}H_{13}ON$ requires N, 6·0; C, 81·5; H, 5·5%). Mixed m.p. with an authentic specimen prepared by the action of hydrogen cyanide on benzylidene-acetophenone[17] showed no depression.

[17] Hann and Lapworth, *loc. cit.*

13. *α-Phenyl-β-benzoyl-propionic acid* (XI ; $R_1 = C_6H_5-$).—The preceding nitrile was hydrolysed as in (11) ; m.p. 152–53°. (Found :† C, 75·6 ; H, 5·4 ; $C_{16}H_{14}O_3$ requires C, 75·6 ; H, 5·5%). This acid was obtained (m.p. 152–53°) by Hann and Lapworth[18] by hydrolysing the nitrile (X ; $R_1 = C_6H_5-$) with conc. sulphuric acid.

14. *α-Benzoyl-β-(3·4-methylene-dioxy-6-nitro-phenyl)-α-β-dibromo-ethane* (II ; $R_1 = CH_2O_2C_6H_2NO_2-$) prepared as in (1) from phenyl-(3·4-methylene-dioxy-6-nitro-styryl)-ketone (I ; $R_1 = CH_2O_2C_6H_2NO_2-$) crystallised from benzene-toluene in pale yellow needles, m.p. 174–75°. (Found : Br, 35·3 ; $C_{16}H_{11}O_5NBr_2$ requires Br, 35·0%). With potassium iodide as in (7) it reformed the chalcone (I ; $R_1 = CH_2O_2C_6H_2NO_2-$).

15. *α-Benzoyl-β-(3·4-methylene-dioxy-6-nitro-phenyl)-α-β-dichloro-ethane* (VII ; $R_1 = CH_2O_2C_6H_2NO_2-$) (3 g.) in acetic acid (50 c.c.) was treated with chlorine (0·7 g.) and diluted with water. The pasty product was kept in contact with sodium bicarbonate solution until it solidified. It recrystallised from benzene-petroleum ether (charcoal) in pale yellow crystals, m.p. 151–52°. (Found : Cl, 19·4 ; $C_{16}H_{11}O_5NCl_2$ requires Cl, 19·3%).

16. *Ethyl-2-(3′·4′-methylene-dioxy-phenyl)-4-phenyl-* Δ^4*-cyclo-hexene-6-one-1-carboxylate* (XII ; $R_1 = CH_2O_2C_6H_3-$).—A mixture of sodium ethylate (0·8 g. Na in 25 c.c. abs. alcohol), aceto-acetic ester (8 g.), (I ; $R_1 = CH_2O_2C_6H_3-$) (10 g.) and alcohol (100 c.c.) was heated under reflux at 80–90° for three hours. The product (13 g.) recrystallised from alcohol-acetone in white needles, m.p. 151–52°. (Found : C, 72·3 ; H, 5·5 ; $C_{22}H_{20}O_5$ requires C, 72·5 ; H, 5·5%).

17. *α-Phenyl-γ-(3·4-methylene-dioxy-phenyl)-propyl-alcohol* (XIII ; $R_1 = CH_2O_2C_6H_3-$).—(I ; $R_1 = CH_2O_2C_6H_3-$) (5 g.) was dissolved in ethyl alcohol (250 c.c.) at 60–65° and the air in the flask containing the solution was expelled by pure hydrogen, after which palladous chloride solution (15 c.c. of 1%) and gum arabic (15 c.c. of 1% solution) were added. The flask was then connected to the hydrogen generator and vigorously shaken. It was difficult to observe the absorption of hydrogen, but after some time the yellow colour disappeared and a colourless solution was obtained. The suspended catalyst coagulated when the reduction was complete. The greater part of the alcohol was removed by distillation and the separated mass was recrystallised from dil. alcohol (yield : 4·5 g) ; m.p. 95–96°. (Found : C, 75·1 ; H, 6·2 ; $C_{16}H_{16}O_3$ requires C, 75·0 ; H, 6·2%).

18. *3-Phenyl-5-(3′·4′-methylene-dioxy-phenyl)-pyrazoline* (XIV ; $R_1 = CH_2O_2C_6H_3-$).—A solution of (I ; $R_1 = CH_2O_2C_6H_3-$) (2 g.) in alcohol (20 c.c.)

[18] *Loc. cit.*

after being heated with 50 per cent. hydrazine hydrate (2 c.c.) at 80° deposited white needles on cooling. These decomposed on drying. The following derivatives were prepared and analysed.

Hydrochloride—pinkish brown crystalline needles ; m.p. 197–98° (Found : Cl, 12·1 ; $C_{16}H_{15}O_2N_2Cl$ requires Cl, 11·7%).

Picrate—recrystallised from alcohol in shining yellow plates ; m.p. 185–86°. (Found :* N, 14·3 ; $C_{22}H_{17}O_9N_5$ requires N, 14·1%).

Acetyl derivative—recrystallised from alcohol in white needles ; m.p. 153–54°. (Found : N, 9·3 ; $C_{18}H_{16}O_3N_2$ requires N, 9·1%). A trace of the pyrazoline dissolved rather slowly in conc. sulphuric acid and the solution did not give a colour with ferric chloride or sodium nitrite solution. When it was reduced by 2·5% sodium amalgam, no odour of ammonia could be detected.

19. 1·3-*Diphenyl*-5-(3′·4′-*methylene-dioxy-phenyl*)-*pyrazoline* (XV; $R_1 = CH_2O_2C_6H_3-$).—A mixture of (I ; $R_1 = CH_2O_2C_6H_3-$) (5 g.) in hot acetic acid (50 c.c.) and phenyl-hydrazine (2·5 g.) after being heated at 90–100° for fifteen minutes deposited on cooling white clusters which were recrystal-lised from alcohol (yield, 5 g.) ; m.p. 129–30°. (Found :* N, 8·2 ; C, 77·1 ; H, 5·5 ; $C_{22}H_{18}O_2N_2$ requires N, 8·2 ; C, 77·1 ; H, 5·3%). The product gave a fluorescent sky-blue colour in chloroform or benzene and was easily soluble in conc. sulphuric acid. The solution gave an intense blue colour with a drop of ferric chloride or sodium nitrite solution. It did not change on boiling with acetic acid. It gave a nitroso-derivative which decomposed when dry.

20. *Oxide of phenyl*-(3·4-*methylene-dioxy-styryl*)-*ketone* (XVI ; $R_1 = CH_2O_2C_6H_3-$).—A solution of (I ; $R_1 = CH_2O_2C_6H_3-$) (20 g.) in a warm mixture of methyl alcohol or rect. spirit (250 c.c.) and acetone (150 c.c.) was cooled to 40° and to the suspension were quickly added hydrogen peroxide (120 c.c. of 20 vol. concentration, *i.e.*, 6%) and 10 per cent. aq. sodium hydroxide (20 c.c.). The whole was shaken for about 15 minutes, when the partly separated chalcone dissolved. The rise in temperature was controlled by cooling under the tap. On cooling a needle-shaped crystalline product separated. A further yield was obtained on diluting the filtrate. The precipitate (18·5 g.) recrystallised from alcohol-acetone in white prismatic needles, m.p. 99–100°. (Found :† C, 71·7 ; H, 4·4 ; $C_{16}H_{12}O_4$ requires C, 71·6 ; H, 4·5%).

21. *Hydrazone of the oxide of phenyl*-(3·4-*methylene-dioxy-styryl*)-*ketone* (XVII ; $R_1 = CH_2O_2C_6H_3-$).—The preceding oxide (2 g.) in alcohol (20 c.c.) was boiled with 50 per cent. hydrazine-hydrate (2 c.c.) for five minutes. The

white crystals (1·6 g.) which separated on cooling were recrystallised from alcohol, m.p. 173–74°. (Found : N, 10·0 ; $C_{16}H_{14}O_3N_2$ requires N, 10·0%). Potassium nitrite in acetic acid did not react with the compound.

22. *3-Phenyl-5-(3′.4′-methylene-dioxy-phenyl)-pyrazole* (XVIII ; R_1= $CH_2O_2C_6H_3$—).—A solution of the preceding hydrazone (XVII ; R_1= $CH_2O_2C_6H_3$—) (2 g.) in alcohol was boiled with sodium ethoxide (0·5 g. sodium in 5 c.c. abs. alcohol), and cooled, when crystalline needles (1·5 g.), m.p. 194–95°, separated and were recrystallised from alcohol. The same product was obtained when the hydrazone was boiled with acetic anhydride. (Found : N, 10·8 ; $C_{16}H_{12}O_2N_2$ requires N, 10·6%).

23. *α-Benzoyl-α-hydroxy-β-methoxy-β-(3·4-methylene-dioxy-phenyl)-ethane* (XIX ; R_1=$CH_2O_2C_6H_3$— ; R′=Me). — To a suspension of the oxide (XVI ; R_1=$CH_2O_2C_6H_3$—) (4 g.) in methyl alcohol (20 c.c.) was added a mixture of methyl alcohol (20 c.c.) and conc. sulphuric acid (5 c.c.) ; and the whole was shaken and warmed to 40°, when it formed a pale yellow solution. On keeping in the refrigerator colourless needles separated. They were washed with water and finally with alcohol (yield 2·5 g.) ; m.p. 117–18°. (Found :† C, 67·7 ; H, 5·4 ; $C_{17}H_{16}O_5$ requires C, 68·0 ; H, 5·3%).

24. *α-Benzoyl-α-hydroxy-β-ethoxy-β-(3·4-methylene-dioxy-phenyl)-ethane* (XIX ; R_1=$CH_2O_2C_6H_3$— ; R′=Et).—Prepared similarly to 21 ; the product did not separate until the solution was diluted, when it formed a paste containing crystals. It recrystallised from alcohol (charcoal) in small colourless prisms, m.p. 93–94°. (Found :† C, 69·2 ; H, 5·9 ; $C_{18}H_{18}O_5$ requires C, 68·8 ; H, 5·7%).

25. *Phenyl-(3·4-methylene-dioxy-benzyl)-diketone* (XX ; R_1=$CH_2O_2C_6H_3$—).—The methoxy-compound (XIX ; R_1=$CH_2O_2C_6H_3$—) (0·6 g.) was heated with sodium acetate (1 g.) in acetic acid (8 c.c.) for two hours at 100° ; the product precipitated by addition of water crystallised from alcohol in yellow needles, m.p. 114–15°.

The same product was obtained when the methoxy-compound was boiled in alcoholic solution for 2–3 minutes with a few drops of aq. sodium hydroxide ; the orange solution was diluted with dilute hydrochloric acid and the precipitate recrystallised from alcohol. (Found : C, 71·3 ; H, 4·4 ; $C_{16}H_{12}O_4$ requires C, 71·7 ; H, 4·5%).

The diketone was, however, best prepared by boiling the alcoholic solution of the oxide (XVI ; R_1=$CH_2O_2C_6H_3$—) with aq. sodium hydroxide for 30 seconds. The red solution was diluted with dilute hydrochloric acid, and the product crystallised from alcohol in yellow needles. The substance turns

pasty after a fortnight, unless kept in a sealed tube. It gives a purple colour with alcoholic ferric chloride.

26. *2-Phenyl-3-(3′·4′-methylene-dioxy-benzyl)-quinoxaline.*—The preceding diketone (0·7 g.) in alcohol (10 c.c.) was boiled with *o*-phenylene-diamine (0·3 g.) for five minutes. The product that separated on cooling recrystallised from alcohol in white needles (yield, 0·8 g.), m.p. 137–38°. (Found: N, 8·2; $C_{22}H_{16}O_2N_2$ requires N, 8·2%).

27. *Phenyl-(3·4-methylene-dioxy-benzyl)-glycollic-acid* (XXI; $R_1 = CH_2O_2C_6H_3-$).—The oxide (XVI; $R_1 = CH_2O_2C_6H_3-$) (10 g.) in alcohol (75 c.c.) was boiled under reflux for four hours with sodium hydroxide (5 g.) in water (15 c.c.) and the solution was diluted with water and filtered. The filtrate was acidified with dilute hydrochloric acid and the precipitate recrystallised from dilute alcohol; white needles, m.p. 149–50° (Yield, 6·2 g.). (Found:† C, 67·0; H, 5·2%; equiv. 290; $C_{16}H_{14}O_5$ requires C, 67·1; H, 4·9%; equiv. 286).

28. *Phenyl-(3·4-methylene-dioxy-benzyl)-ketone* (XXII; $R_1 = CH_2O_2C_6H_3-$). —The preceding acid (5 g.) in warm acetic acid was treated with potassium dichromate (3 g.) dissolved in the minimum quantity of water and then diluted with acetic acid. After one minute, the solution was diluted with water and the light green ppt. was filtered and extracted with acetone. The extract after removal of the solvent gave a paste which solidified after keeping at 0° for two days. It recrystallised from pet. ether in small colourless needles; m.p. 70–71° (yield, 2 g.).

The substance has previously been prepared (m.p. 71–72°) by Tiffeneau and Lévy[19] by the distillation of the oxide of (3–4–methylene-dioxy-styryl)-benzene.

29. *Oxide of phenyl-(3·4-methylene-dioxy-6-nitro-styryl)-ketone* (XVI; $R_1 = CH_2O_2C_6H_2NO_2-$).—Prepared as in (20) from (I; $R_1 = CH_2O_2C_6H_2NO_2-$) but the present mixture was shaken for a longer time with slight warming at intervals, and only acetone was used as the solvent. It was difficult to obtain the oxide pure, owing to the insolubility of both the chalcone and its oxide, and it was preferably prepared by the gradual addition at 0° of an alcoholic solution of sodium alcoholate (3 g. Na in 50 c.c. alcohol) to a mixture of *ω*-bromo-acetophenone (20 g.), 6-nitro-piperonal (20 g.) and alcohol (200 c.c.). The oxide (27 g.) separated and was recrystallised from acetone; pale yellow needles, m.p. 159–60°. (Found*: N, 4·7; $C_{16}H_{11}O_6N$ requires N, 4·5%).

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[19] *Compt. rend.*, 1930, **190**, 1510.

30. *Phenyl-β-chloro-α-hydroxy-β-(3·4-methylene-dioxy-6-nitro-phenyl)-ethyl-ketone* (XXIII; $R_1 = CH_2O_2C_6H_2NO_2-$).—The red solution obtained by passing dry hydrogen chloride into a suspension of the preceding oxide in acetic acid cooled in water, was diluted with water after saturation (10 minutes). The precipitated chlorohydrin recrystallised from benzene-pet. ether (charcoal) in pale yellow crystals; m.p. 183–84°. (Found: Cl, 10·5; $C_{16}H_{12}O_6NCl$ requires Cl, 10·2%).

Similar treatment of (XVI; $R_1 = CH_2O_2C_6H_3-$) with hydrogen chloride gave a pasty substance which was not investigated further.

31. *Acetyl derivative of the hydrazone of phenyl-(3·4-methylene-dioxy-6-nitro-styryl)-ketone* (XXIV; $R_1 = CH_2O_2C_6H_2NO_2-$).—A solution of (I; $R_1 = CH_2O_2C_6H_2NO_2-$) (2 g.) in acetic acid (25 c.c.) was heated at 100° with 50 per cent. hydrazine hydrate (3 c.c.) for ten minutes. The ppt. separating on cooling (2 g.) crystallised from acetone in white needles, m.p. 244–25°. (Found :† C, 60·9; H, 4·2; $C_{18}H_{15}O_5N_3$ requires C, 61·1; H, 4·3%). A solution of the substance in conc. sulphuric acid does not give a colour either with ferric chloride or sodium nitrite solution.

32. *Phenyl-hydrazone of phenyl-(3·4-methylene-dioxy-6-nitro-styryl)-ketone* (XXV; $R_1 = CH_2O_2C_6H_2NO_2-$). A mixture of (I; $R_1 = CH_2O_2C_6H_2NO_2-$) (5 g.) in acetic acid (50 c.c.) and phenyl-hydrazine (2 g.) was heated at 100° for ten minutes. The red ppt. (6·6 g.) obtained on addition of dil. hydrochloric acid recrystallised from alcohol-acetone in red needles, m.p. 159–60°. (Found :* N, 11·1; $C_{22}H_{17}O_4N_3$ requires N, 10·9%). The substance dissolved slowly in concentrated sulphuric acid with the formation of colour; and the resulting solution did not give a colour with ferric chloride.

33. *1·3-Diphenyl-5-(3′·4′-methylene-dioxy-6′-nitro-phenyl)-pyrazoline* (XXVI; $R_1 = CH_2O_2C_6H_2NO_2-$).—The preceding phenyl-hydrazone was boiled for an hour with acetic acid. The orange-yellow ppt. obtained on cooling the solution was recrystallised from benzene-petroleum ether, m.p. 203–204°. (Found: N, 11·1; $C_{22}H_{17}O_4N_3$ requires N, 10·9%). It dissolved at once in conc. sulphuric acid and gave Knorr's pyrazoline reaction.

34. *1·3-Diphenyl-5-(3′·4′-methylene-dioxy-6′-nitro-phenyl)-pyrazole* (XXVII; $R_1 = CH_2O_2C_6H_2NO_2-$).—The preceding pyrazoline (0·5 g.) in alcohol (20 c.c.) was heated under reflux for one hour with silver nitrate (1 g.) in water (2–3 c.c.) and the liquid filtered from separated silver and undissolved matter. The filtrate on dilution with water gave a precipitate which crystallised from acetone-alcohol in yellow needles, m.p. 163–64°. (Found :* N, 10·8; C, 68·6; H, 4·0; $C_{22}H_{15}O_4N_3$ requires N, 10·9; C, 68·5; H, 3·9%).

It was better prepared by treating the oxide (XVI ; $R_1 = CH_2O_2C_6H_2NO_2-$) in hot acetic acid, with phenyl-hydrazine. The resulting pale yellow solution was poured into dil. hydrochloric acid and the pale yellow ppt. recrystallised from acetone-alcohol in yellow needles, m.p. 163–64°.

Note.—Micro-analyses of the compounds marked (*) were carried out by Dr. J. N. Ray of Lahore, and those marked (†) were made in Germany by Dr. Fischer and by Dr. Schœller.

SOME NEW FEATURES IN THE RAMAN SPECTRA OF CARBON AND SILICON TETRACHLORIDES.

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1. Introduction.

The Raman spectrum of CCl_4 has been the subject of numerous papers.[1] The great intensity of the lines observed with this substance, the appearance of several anti-stokes components and the striking differences in the state of polarisation of the radiations, are some of the features which make the case one of special experimental interest. From the theoretical standpoint, the chemically indicated tetrahedral symmetry of the molecule makes the comparison of the results to be expected from dynamical theory with those actually observed a matter of considerable importance. Classical mechanics indicates that a molecule with five atoms should, in general, possess nine characteristic frequencies. In the case of CCl_4 and other molecules with tetrahedral symmetry, however, only four out of the nine frequencies are distinct—one being single (the total symmetric vibration) (ν_1), one doubly degenerate (ν_2) and two triply degenerate (ν_3 and ν_4). All the four modes of vibration are Raman-active so that one would expect four lines in the Raman spectrum of CCl_4. Actually, however, the triply degenerate vibration ν_4 in CCl_4 is observed to be split up into a pair of lines of equal intensity. Moreover, a fifth line (faint and diffuse) has been observed in the Raman spectrum of CCl_4 which is found to correspond roughly to the octave of ν_4. The splitting of the fourth frequency has been attributed by Fermi[2] to a "quasi-degeneracy" arising from the fact that the frequency which is split up happens to be almost exactly equal to the sum of two other fundamental frequencies, $\nu_4 \sim (\nu_1 + \nu_3)$. This gives rise to a coupling of the terms which, according to wave mechanics, leads to splitting. Another interesting feature of the Raman spectrum of CCl_4 is the fine structure of the Raman lines ν_1, ν_2 and ν_3. This has been studied in some detail by Langseth.[3] Since chlorine consists of two different isotopes of masses 35 and 37 with a relative abundance ratio 3 : 1, the substance CCl_4 is a mixture of five different kinds of molecules, CCl_4^{35}, $CCl_3^{35}Cl^{37}$, $CCl_2^{35}Cl_2^{37}$, $CCl_3^{35}Cl^{37}$ and CCl_4^{37} which occur in the proportion $31{\cdot}6 : 42{\cdot}2 : 21{\cdot}1 : 4{\cdot}7 : 0{\cdot}4$. The total-symmetric

vibration should therefore consist of five close components with a relative separation of 3·15 cm.$^{-1}$ and with intensities in the above ratio. The presence of the first three components with the expected order of intensity and separation has been recorded by Langseth.

Investigations on $SiCl_4$[2] are not so numerous. The Raman spectrum of this substance has been found to show three strong lines corresponding to ν_1, ν_2 and ν_3 and a broad and diffuse line corresponding to ν_4.

The author has undertaken a careful study of the Raman spectra of these two substances, and has succeeded in getting some new results which are recorded in the present paper.

2. *Experimental.*

Two different instruments have been employed in the present investigation for the study of the Raman spectra:

(i) A Hilger two-prism spectrograph of great light-gathering power giving a dispersion of about 25 Å/mm. in the λ 4358 region.

(ii) A spectrograph of Littrow model, with two glass prisms of large size, one 60° and the other 30°, also supplied by the firm of Adam Hilger Ltd. The dispersion in the region λ 4358 is about 10 Å/mm. In spite of its lesser light-gathering power, well-exposed Raman spectra taken with this instrument are found to show many finer details which are not so strikingly brought out in the pictures with smaller dispersion.

Ilford hypersensitive panchromatic plates were employed to photograph the Raman spectra with the first instrument, and an exposure of about 10 to 12 hours was sufficient to get well-exposed pictures with a slit width of 40 μ. With the instrument of higher dispersion, the time of exposure required varied from 40 to 50 hours. Ilford "golden isozenith" plates with special backing were used in this case.

The liquids employed were very pure chemicals, and special care was taken to free them from dust by repeated slow distillation in vacuum. Wood's arrangement was used for photographing the Raman spectra. The Raman tubes were of pyrex glass with fused on end window, and contained the dust-free liquids sealed off in vacuum. The illumination was from a quartz mercury lamp placed in direct contact with a water jacket surrounding the Raman tube. Concave reflectors of polished aluminium one below the tube and the other above the arc served to enhance the illumination. For making accurate measurements of the modified lines, an iron arc comparison

spectrum was photographed at the centre of the Raman spectrum on all the plates.

3. Results.

The frequency shifts were determined by direct measurement on the photographic negatives using a Hilger cross-slide micrometer reading correct to ·001 mm. The results are correct to ±1 wave number in the case of the photographs taken under high dispersion, which alone were used for measurement. All the spectral details present in the plates taken under high dispersion could also be recognised in the photographs taken with the low dispersion instrument. The results of measurement are listed in the tables below :

TABLE I. CCl_4.

Exciting line	Raman line (ν) cm.$^{-1}$	$\Delta\nu$ cm.$^{-1}$	Exciting line	Raman line (ν) cm.$^{-1}$	$\Delta\nu$ cm.$^{-1}$
4358 Å	21400	1538	4047 Å		
$\nu = 22938$	22147·5	790·5	$\nu = 24705$	23916·3	788·7
	22176·1	761·9		23942·3	762·7
	22479·2	458·8		24246·3	458·7
	22504·0	*434·0*		24271·0	*434·0*
	22623·4	314·6		24390·5	314·5
	22719·6	218·4		24487·0	218·0
	22793·0	*145·0*			
	23156·2	−218·2		24922·0	−217·0
	23250·6	−312·6		25019·3	−314·3
	23396·8	−458·8		25164·9	−459·9

TABLE II. $SiCl_4$.

Exciting line	Raman line (ν) cm.$^{-1}$	$\Delta\nu$ cm.$^{-1}$	Exciting line	Raman line (ν) cm.$^{-1}$	$\Delta\nu$ cm.$^{-1}$
4358 Å	22327	611	4047 Å	24092	613
$\nu = 22938$	22498	*440*	$\nu = 24705$	24264	*441*
	22517	421		24283	422
	22716·5	221·5		24485	220
	22787	151		24556	149
	23089·5	−151·5		24854	−149
	23160	−222		24925	−220
	23361	−423		25130	−425

The mean frequency shifts with visual estimates of intensity are given in the following table:

TABLE III.

CCl_4		$SiCl_4$	
$\Delta\nu$ (cm.$^{-1}$)	Intensity	$\Delta\nu$ (cm.$^{-1}$)	Intensity
145·0 $= (\nu_1 - \nu_3)$	0		
$217·9 = \nu_2$	8	$150·0 = \nu_2$	5
$314·0 = \nu_3$	8	$221·0 = \nu_3$	5
434·0 $= 2\nu_2$	0	$423·0 = \nu_1$	10
$459·0 = \nu_1$	10	*440·5* $= 2\nu_3$	0
762·3, 789·6 $= \nu_4$	3	$612·0 = \nu_4$	2 (broad & diffuse)
$1538·0 = 2(\nu_1 + \nu_3)$	½ (broad & diffuse)		

4. Discussion of Results.

It is well known that Raman spectra are simpler in their structure than the corresponding infra-red spectra. Whereas the infra-red spectra are characterised by the appearance of numerous overtones, these occur but seldom in the Raman effect and even so only with very feeble intensity. The only case in which an overtone has been definitely observed in the Raman spectrum is that of CCl_4 about which mention has been already made. Several faint lines in the Raman spectrum of benzene are classified as overtones and combinational tones[5] although the assignment in these cases is by no means unique.

In the Raman spectrum of CCl_4, we have been able to recognise two faint lines in addition to those already reported. The fact that these two lines have so far escaped notice is not surprising when one considers their extreme faintness. Indeed, even the stronger line at 1538 cm.$^{-1}$ has not been observed by some workers who have studied the Raman spectrum of CCl_4 under high dispersion.* The faint line at 434 cm.$^{-1}$ is to be interpreted as the octave of ν_2 (=217·9 cm.$^{-1}$) and its appearance is in all probability due to its proximity to the total-symmetric vibration frequency ν_1 (=459 cm.$^{-1}$). The new line observed at 145 cm.$^{-1}$ appears to be a differential tone arising from ν_1 (=459 cm.$^{-1}$) and ν_3 (=314 cm.$^{-1}$), the same two the summational of which causes the splitting of the fourth frequency ν_4, and the octave of whose summational comes out as the faint diffuse line at 1538 cm.$^{-1}$ That this faint line does not coincide with any of the Raman lines excited by the companions of 4358, that it does not appear in the Raman spectra of other substances such as PCl_3, and that it is unmistakably present in the photographs taken with two different instruments, make it absolutely certain that it is quite genuine.

Regarding the principal Raman lines of CCl_4 the following remarks may be made. As has been pointed out by Langseth, the Raman lines when photographed under high dispersion are far from being sharp. In the present work, since the object was not the study of the fine structure of the lines, it was not considered worthwhile to use a particularly narrow slit. The Raman spectrum of CCl_4 taken with the high dispersion instrument is reproduced in Fig. 1 in the Plate. It will be noticed that the first two lines (ν_2 and ν_3) have a similar structure. The intensity is maximum at the centre and fades off symmetrically towards either side. The symmetrical vibration ν_1 shows the unresolved isotopic structure. It is sharp and intense towards

* There is no mention of it in Langseth's paper, and Mesnage has said that he was unable to find it even in his most intense pictures.

the red side and weak and diffuse towards the side of shorter wave-length. Its width extends over a range of about 8 wave numbers. A new and significant observation regarding this line is the presence of a clear wing to its red side sharply separated from the line. The author does not find any mention of such a wing in Langseth's paper. The fact that such a wing is entirely absent for the other two Raman lines deserves mention. Its origin does not seem clear.

The new faint line at 440·5 cm.$^{-1}$ observed in the Raman spectrum of $SiCl_4$ appears to be the octave of the fundamental frequency ν_3 (= 221 cm.$^{-1}$) and it seems justifiable to extend the same reasoning which has been suggested in the case of CCl_4 to explain its appearance. Of the principal Raman lines of $SiCl_4$, the first (ν_2) is broad, the second (ν_3) is more sharp and the symmetric vibration (ν_1) is the sharpest of all. ν_4 is broad and diffuse with a fairly sharp edge towards the shorter wave-length side. This broadening might probably be due to the fact that the relation $\nu_4 \sim (\nu_1 + \nu_3)$ which causes the splitting of ν_4 in the case of CCl_4, is very roughly satisfied even in the case of $SiCl_4$.

In conclusion, the author wishes to express his respectful thanks to Professor Sir C. V. Raman for his kind interest and suggestions in the course of this work.

5. *Summary.*

The Raman spectra of CCl_4 and $SiCl_4$ have been examined under low and high dispersion. In both cases a faint line has been observed close to the line corresponding to the total symmetric vibration. This faint line has a frequency shift of 434 cm.$^{-1}$ in the case of CCl_4 and is interpreted as the octave of the fundamental frequency 217·9 cm.$^{-1}$ The corresponding line in the case of $SiCl_4$ shows a frequency shift of 440·5 cm.$^{-1}$ and is interpreted as the octave of the fundamental frequency 221 cm.$^{-1}$ It is pointed out that the appearance of the octave in these cases might probably be due to its proximity to the total-symmetric vibration frequency which is respectively 459 cm.$^{-1}$ and 423 cm.$^{-1}$ in the case of CCl_4 and $SiCl_4$. An additional faint line with a frequency shift of 145 cm.$^{-1}$ has been observed in the Raman spectrum of CCl_4 which is interpreted as a differential tone arising from the fundamental frequencies 459 cm.$^{-1}$ and 314 cm.$^{-1}$, the summational of which causes the splitting of the fourth frequency, and the octave of whose summational appears as a faint broad line at 1538 cm.$^{-1}$ The broadening of the fourth frequency in the case of $SiCl_4$ might be due to a cause similar to that which causes the splitting of the fourth frequency in the case of CCl_4. The total symmetric vibration in the case of CCl_4 shows a well-defined wing to its red side, sharply separated from the principal line.

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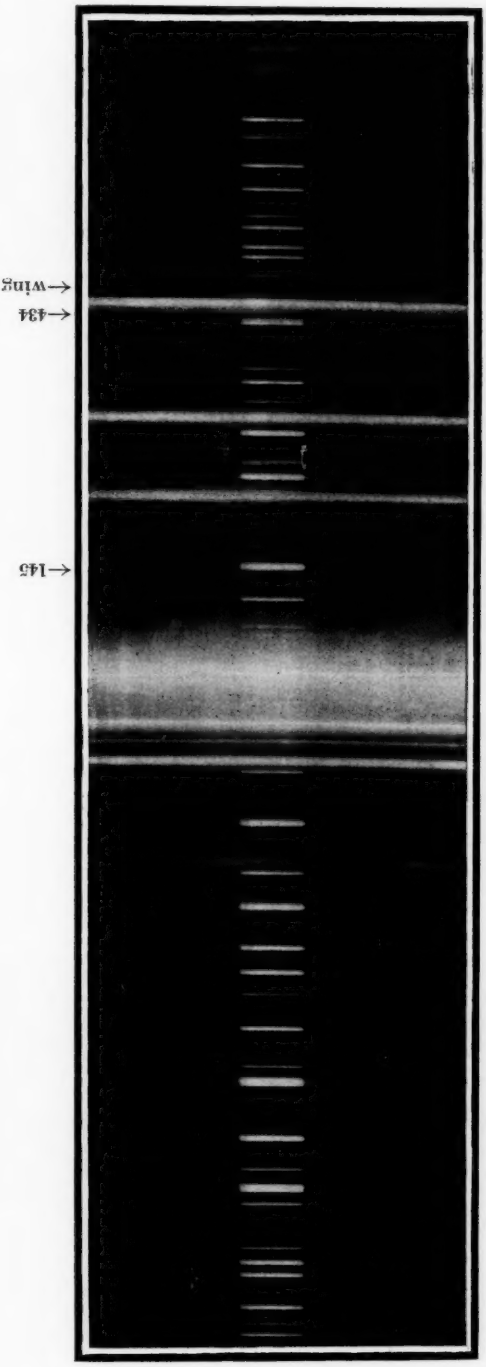

FIG. 1. Raman Spectrum of CCl_4.
(Littrow Spectrograph)

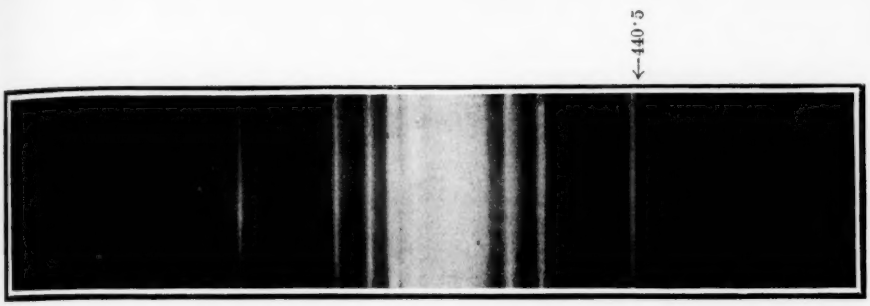

FIG. 2. Raman Spectrum of $SiCl_4$.
(Two-prism Spectrograph)

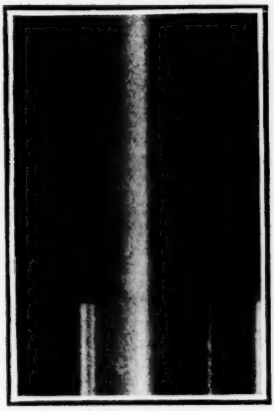

FIG. 3. 459 cm.$^{-1}$ line of CCl_4 showing unresolved isotope structure, the wing to its right and the octave line at 434 cm.$^{-1}$ to its left.

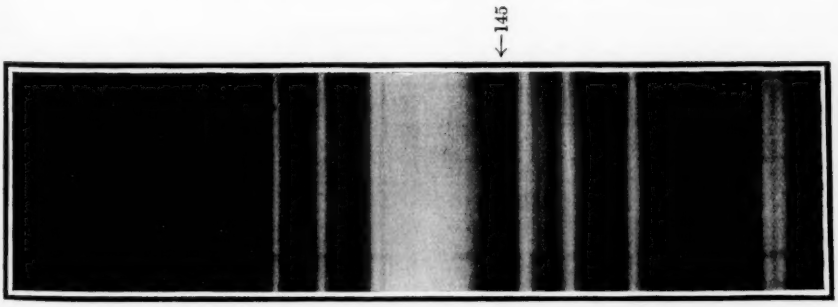

FIG. 4. Raman Spectrum of CCl_4.
(Two-prism Spectrograph)

THE FLUORESCENCE OF RUBY, SAPPHIRE AND EMERALD.

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1. Introduction.

The remarkably brilliant crimson luminescence of ruby was at first observed by Edmond Becquerel[1] by irradiation with sunlight and was later on, the subject of detailed investigations at the hands of several investigators notably Lecoq de Boisbaudran,[2] Du Bois and Elias,[3] Schmidt,[4] and Mendenhall and Wood.[5] As has been observed by these authors, ruby furnishes an interesting example of a solid yielding sharp lines of luminescence and its spectrum consists of two intense lines at 6926 and 6942* accompanied by other lines or bands on either sides. The cathodo-luminescence of ruby was investigated by Sir William Crookes[6] and his results agree well with those obtained by visible light. The origin of this luminescence was the subject of prolonged controversy beween Becquerel and Crookes on the one hand and Lecoq on the other. The former authors maintained that the agent causing luminescence was alumina while the latter insisted that the small trace of chromium present was responsible for the same. The detailed investigations of Wiedmann and Schmidt[7] and later by Schmidt[8] succeeded in showing that carefully fractionated pure alumina is non-luminescent and a small trace of chromium (1 : 10,000) is sufficient to make the lines appear intensely. Recently, Tanaka[9] showed that almost all the lines of the ruby coincide with the chromium series discovered by him and from that he was led to conclude that the small trace of chromic oxide present in ruby is the cause of its luminescence.

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1 Becquerel, E., *Ann. de Chim. et Phys.*, 1859, **57**, 125; 1861, **62**, 90.
2 Lecoq de Boisbaudran, *Compt. Rend.*, 1887, **103**, 1107, 1224; 1824, **104**, 330, 478, 554.
3 Du Bois, H., and Elias, J., *Ann. d. Phys.*, 1908, **27**, 233; 1911, **35**, 635.
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5 Mendenhall, E. C., and Wood, R. W., *Phil. Mag.*, 1915, **30**, 316.
* The numbers in this and the subsequent pages denote the wavelengths in Ångstrom units.
6 Crookes, W., *Chem. News*, 1887, **55**, 25 and **56**, 59.
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8 Schmidt, G. C., *Loc. cit.*
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Alumina in solid solutions with the oxides of other metals like copper, manganese, beryllium, samarium, etc., is also known to exhibit fluorescence,[10] the colour of which varies with the active metal used. The luminescence of alumina in the form of aluminates or silicates in the natural state, namely, topas, spinel and smaragd, etc., has also been investigated qualitatively but their complete spectral character and its bearing on the origin of luminescence has not been fully studied.

In continuation of some unpublished work by Mr. Bhagavantam, the author has investigated the fluorescence spectra of the emerald, sapphire and ruby with a Fuess glass spectrograph of large aperture and having a dispersion of 100 Å per millimetre in the 6900 region. A pyrex mercury arc as well as a carbon arc has been used as sources of illumination. A deep blue solution of cupro-ammonium sulphate surrounding the solid cut off the radiations of the source beyond 5500, where the fluorescence of these crystals appear. Ilford hypersensitive panchromatic plates, H and D 2500, are used for photographing the spectrum. The fluorescence of sapphire shows close similarity to the well-known spectrum of ruby ; but the emerald, which however belongs to the beryl family, possesses striking dissimilarities in its spectrum though some general features characteristic of the ruby are also noticeable in this case.

2. *Results.*

Emerald.—The most interesting of the substances investigated is the emerald. It was available in the form of round beads of about 1·5 cm. to 2·5 cm. in diameter and in different tones of colour ranging from greyish green to pale green. These beads possess a fairly constant density of 2·66. A transparent green crystal in the form of a cut jewel with polished faces, which gives almost the same spectrum as the beads, has a refractive index of 1·5751 for the D-lines of sodium. A chemical analysis† of one of the beads gives the percentage composition of the mineral as 3 BeO. Al_2O_3. 6 SiO_2 with 0·3% of iron and an easily detectable quantity (about 0·25%) of chromium as well as small traces of rare earth elements. The fluorescence is very weak in these beads, an exposure of about twenty-four hours being required to obtain a fairly intense spectrum under the most favourable circumstances while the ruby has yielded the main lines in a minute. Its spectrum consists of two intense and sharp lines at 6806 and 6837, the latter being stronger and broader than the former and a system of diffuse bands on either sides. In order to understand which part of the spectrum of the source is responsible

[10] *Handbuch der Exptl. Phys.*, 1928, **23**, Part 1, p. 425.

† The chemical analysis was carried out by Mr. N. Jayaraman of the Department of General Chemistry of this Institute to whom the author's best thanks are due.

for this fluorescence, the intense lines of the mercury arc have been isolated by suitable filters and used separately for excitation and the fluorescence appears equally well and unchanged in character for the 4046, 4358 and 5461 radiations of the arc. The wave-lengths of the lines are measured by comparison with the iron arc spectrum and the mercury arc lines and are classified in Table I together with their relative intensities. The wave-lengths given for the two intense lines at 6806 and 6837 are correct to $\pm$ 1 Å. An enlarged picture of the spectrum is reproduced in Fig. 1 of the accompanying Plate. In view of the characteristic dissimilarity of the spectrum of emerald from that of ruby, the author has also examined fairly transparent pieces of a bluish green and a deep green (smaragd) beryl. According to chemical analysis, also carried out by Mr. Jayaraman, the bluish green crystal has a structure 3 BeO. Al_2O_3. 6 SiO_2 but contains about 3% iron and only a very much smaller percentage of chromium than the emerald, barely detectable during the analysis. It has yielded no fluorescence even on prolonged exposure of more than forty-eight hours though the Raman line[11] 647 cm.$^{-1}$ appears in four hours. The deep green crystal possesses an intense fluorescence between 4950 and 5450 in agreement with the observations of some earlier workers for beryl.[12] The significance of these results are discussed in a later section.

Sapphire.—This was available in the form of light blue beads having a density of 3·95, thus evidently belonging to the corundum family. Blue crystals possessing deeper shades of colour are also examined in the form of cut stones and all of them have given an identical spectrum. The fluorescence, however, being extraordinarily feeble, very long exposures of about forty-eight hours are required to record the spectrum and this, perhaps, accounts for the absence of any investigation on the luminescence of this mineral. The spectrum consists of two intense and sharp lines at 6927 and 6942 and a series of bands, resembling the spectrum of ruby and is illustrated in Figs. 4 and 6. The results are given in Table I along with those of emerald.

Ruby.—In order to furnish a comparison for the spectra of the two former substances, the fluorescence of a few beads of natural ruby of density four have also been examined. An exposure of about four hours has yielded a very intense spectrum showing a number of interesting features which have not been observed previously. It may be mentioned that in the previous investigations of ruby instruments of large dispersion of about 3 Å per millimetre but only poor light-gathering power have been used by Mendenhall

[11] Nisi, H., *Proc. Phys. Math. Soc. Jap.*, S., 1932, **14**, 214.

[12] Gmelin's *Handbuch der Anorg. Chem.*, 1930, **26**, Be. 21.

TABLE I.

(*a*) *Emerald at* 35° *C.* (*b*) *Sapphire at* 35° *C.*

Wavelength in A.U.	Intensity	Wavelength in A.U.	Intensity
		7130	weak broad band
6946	very weak and diffuse band	7060	very weak band
6908	weak, diffuse band	6992	weak band
6837	very strong line	6942	very strong line
6806	strong sharp line	6927	strong sharp line
6736	strong band	6802	broad diffuse band
6633	medium band	6753	weak band
6578	weak band	6690	medium band
		6592	strong narrow band

and Wood and Du Bois and Elias. While the latter authors recorded a large number of lines on either sides of the intense doublet at 18° C., Wood and co-worker[13] were unable to reproduce their results at 23° C. With an exposure of *one minute* at a temperature of about 35° C. the author has been able to record the two lines reported by Wood and his co-worker with good intensity. At longer exposures many more lines and bands appear, some of which are observed for the first time. That Wood and Mendenhall did not obtain any but the most intense lines, is perhaps due only to the low intensity of the spectrograph and short time of exposure. The results obtained by the author are given in Table II together with those of the above authors. Besides the bands recorded by Du Bois and Elias, four new bands with centres approximately at 7089, 7164, 7222 and 7266 in the red end and three bands at 6650, 6495 and 6430 and a fairly sharp line at 6814 superposed by a weak band have been observed. These bands are also followed by a continuous spectrum between 6100 and 6900 which is especially noticeable in the over-exposed picture (Fig. 3). Because of the low dispersion of the spectrograph used, the sharp lines between 6946 and 7016 reported by the earlier workers are not resolved in the author's spectrum and have appeared only as a blackening in the Plate. Fig. 5 in the accompanying Plate shows that the lines 6927 and 6945 are of unequal intensity as they are in sapphire. Fig. 2 gives an intense picture showing all the lines and bands clearly, particularly the

[13] Mendenhall and Wood, *Loc. cit.*

TABLE II.

Ruby.

Author—35°C.		Du Bois and Elias—18°C.		Mendenhall and Wood—23°C.	William Crookes
Wavelength in A.U.	Intensity	Wavelength in A.U.	Intensity	Wavelength in A.U.	Wavelength in A.U.
7266	very weak band	....			
7222	very weak band	....			
7164	weak band	....			
7125	medium narrow band	7130	diffuse darkening		
7089	medium narrow band	....	dark space		
7059	medium narrow band	7060	diffuse darkening		
7027	medium sharp line	7046	narrow band		
6992	weak sharp line	7016	narrow band		
Unresolved blackening		group of lines	(diffuse)		
6945	very strong sharp line	6941	very strong band	6946	6942
6927	strong sharp line	6926	strong band	6932	6937
6814	weak sharp line (very weak continuous spectrum superposed)	....			
6791	weak sharp line	6790	narrow band		
6753	medium diffuse band	6760	band		
6690	strong broad band	6690	diffuse band		6707
6650	weak diffuse band	....			
6592	strong narrow band	6590	weak band		6598
6495	weak band	....			
6430	very weak band	....			6514 (approximate centre of continuous spectrum)
Continuous spectrum between 6100 and 6900		....			

line at 6814 which almost coincides with one of the emerald lines. Fig. 3 which is an over-exposed spectrum shows the new bands observed in the red end as well as the continuous spectrum.

3. *Discussion of Results.*

Just as the ruby and the sapphire differ very little in their physical properties such as density, refraction and crystal structure, a close similarity exists also in their fluorescence spectra as can be seen from Figs. 2 and 4. According to Stillwell,[14] the blue colour of the natural sapphire is due to *chromous oxide* while the red colour of ruby is caused by a small percentage of *chromic oxide*. On the other hand there are some[15] who presume that the blue colour is entirely due to ferric or titanium oxide and that chromium is completely absent in it. Artificial sapphire resembling the natural stone has also been successfully prepared by fusing a mixture having a composition[16] of 98% Al_2O_3, 1·5% Fe_3O_4 and 0·5% TiO_2. The only differences observed by the author in the fluorescence spectra of ruby and sapphire are : (1) the fluorescence in sapphire is extremely feeble as compared with that of ruby, (2) the doublets in ruby at 6791 and 6814 as well as at 7059 and 7089 are replaced by bands in sapphire. While it is not justifiable to draw any conclusion from these regarding the state and nature of impurities causing colouration in them, it is to be inferred that in both the materials the same agent is responsible for fluorescence and as is pointed out in the beginning, chromium is present in some form or other in both the stones.

In the case of the emerald in which alumina is largely diluted by the presence of the oxides of beryllium and silicon, the fluorescence spectrum is very different from that of ruby as can be seen from Figs. 1 and 2. There are also some striking similarities in their spectrum. The prominent lines of the emerald spectrum at 6806 and 6835 are sharp and it is remarkable that these lines almost coincide with the weak doublet at 6792 and 6814 in ruby. The occurrence of diffuse bands on either sides of these lines is also a feature in common with the spectrum of the latter. These broad bands bear a resemblance to the diffuse bands of ruby at temperatures higher than 200° C. and may sharpen at lower temperatures. It may be concluded from these that the luminescence in emerald is also, probably, caused by chromium. The fact that beryl containing very little or no chromium does not give this characteristic line spectrum, lends support to this view. But it is difficult to understand why the strong doublet at 6926 and 6945 in the ruby should be suppressed almost completely and the doublet at 6792 and 6824 should appear a little shifted as the most prominent lines in emerald. The line at 6792 appears also intensely in the cathodo-luminescence of spinel[17](magnesium

[14] Stillwell, C. W., *J. Phys. Chem.*, 1926, **30**, 1441.
[15] Krans and Holden, *Gem Materials*, 1925, 100.
[16] Verneuil, A., *Compt. Rend.*, 1910, **150**, 186.
[17] Crookes, W., *Loc. cit.*

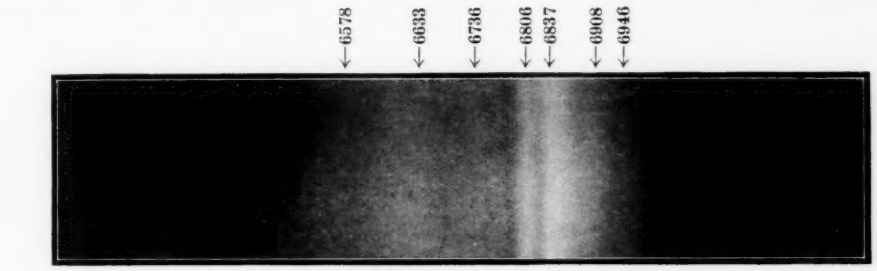

FIG. 1. Emerald

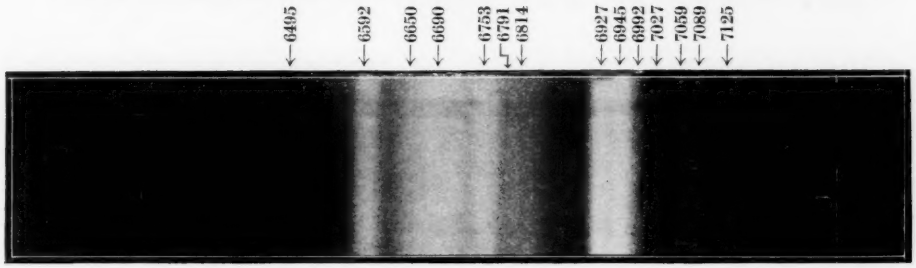

FIG. 2. Ruby (1 hour)

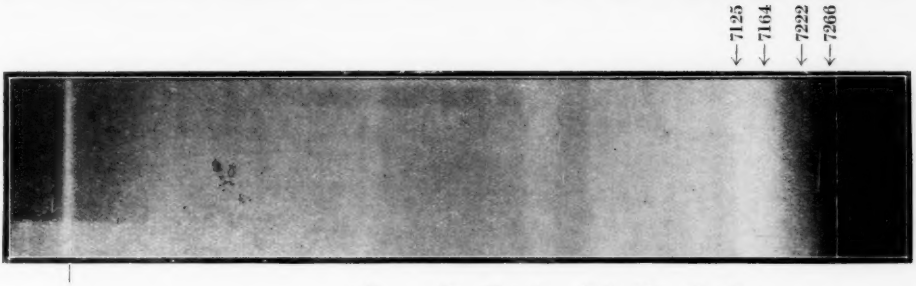

FIG. 3. Ruby (4 hours)

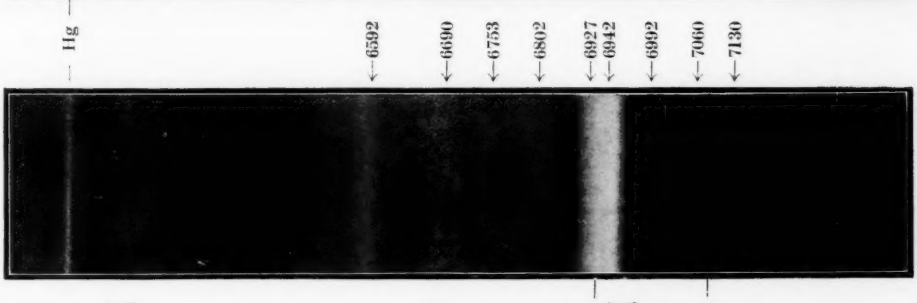

FIG. 4. Sapphire (pale blue)

Sapphire (deep blue)

FIG. 5. Ruby (1 min.)

FIG. 6.

aluminate). A proper explanation of this cannot be given at this stage; but it is possible that the presence of the other oxides in the crystal is responsible for this behaviour. A study of the luminescence of alumina fused with chromic oxide and a large percentage of other oxides may throw light on this problem. It would also be of interest to examine the fluorescence of emerald at various temperatures, particularly at the liquid air temperature and compare the behaviour with that of ruby under identical circumstances. The author hopes to undertake work on these lines soon and the results will be communicated in due course.

In conclusion, the author desires to express his grateful thanks to Prof. Sir C. V. Raman, for his keen interest and constant encouragement in the course of the work as well as for kindly placing his valuable collection of gems at the disposal of the author.

Summary.

The photo-luminescence of natural crystals of ruby, sapphire and emerald (beryl) has been studied at room temperature with a Fuess spectrograph of high light-gathering power. The ruby has yielded a number of new bands which have not been obtained hitherto. The spectrum of sapphire corresponds closely to that of ruby but with slight differences. The spectrum of emerald consists of two sharp lines at 6806 and 6835 accompanied by other diffuse bands and is compared with that of ruby. The fluorescence in sapphire and emerald is also discussed with respect to the origin of luminescence in them. Photographs of the spectra illustrate the paper.

ON THE THEORY OF LIQUIDS—V.

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1. *Introduction.*

The theory under discussion in this series of papers[1] is a modification and extension of Edser's theory[2]; it considers a liquid as composed of a number of simultaneously attracting and repelling force centres or molecules, each of which vibrates within a spherical space of diameter σ, which is kept free from other molecules by the thermal motion of the occupying molecule. This, it should be emphasised, represents a statistical effect; occasionally a molecule will be associated with a greater or even a smaller space, but usually there will be no other molecules within the associated space of diameter σ, and outside it there will be uniform distribution of molecular centres. Near the melting-point, the translational motion of a molecule will be small compared with the vibratory motion within its spherical space.

σ is considered to vary with the temperature, and not as Edser assumed to be independent of it. It is calculated by supposing the spaces are closely packed so that it is related to V by the equation

$$N\sigma^3 = V\sqrt{2} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (1)$$

It is also assumed that σ, while it varies with temperature, is relatively independent of small alterations in other variables; for example, it is assumed that

$$\left(\frac{d\sigma}{dT}\right)_V = \left(\frac{d\sigma}{dT}\right)_p \quad .. \quad .. \quad .. \quad .. \quad (2)$$

In other words, the space which it keeps clear by its thermal motion is an intrinsic property of a molecule at a given temperature.

A number of formulæ for various properties of liquids have been developed in the previous papers. In Parts, I, II, III, the equations were of the type which related various properties of a liquid one to another, but one property of a liquid, say the density, had to be known before the remainder could be calculated. In Part IV, equations were deduced for the

[1] *Ind. J. Physics*, 1934, **8**, Part I, 521; *Proc. Ind. Acad. Sciences*, 1934, **1**, Part II, 105; 1935, **1**, Part III, 795; 1935, **2**, Part IV, 1; see also *Current Science*, 1934, **3**, 23; 1935, **3**, 347, 550.

[2] *Brit. Assoc. Fourth Report Coll. Chem.*, 1922, 40.

forces on a particle vibrating in a spherical space under the influence of attractive and repulsive forces between the particle, and uniformly distributed matter outside the spherical space.

The object of this paper, which is intended to be the last of the series, is to give a summarised presentation of the theory, with an outline of the derivation and application of the principal equations, and to show how with the aid of the equations derived in Part IV, the properties of a liquid could be calculated, if the temperature, and the fundamental properties of a molecule, the forces which it generates, are known.

2. *General Considerations.*

It is assumed that we are dealing with a liquid of low vapour pressure near the melting-point. The translational motions of the molecules are neglected, and each molecule is taken to be vibrating within its associated spherical space of diameter σ. It attracts and repels other centres by forces which are given respectively by $\frac{\mu}{\gamma^m}$ and $\frac{\lambda}{\gamma^n}$. It is assumed that when the molecule is at the centre of its associated space, the effect of the short-range repulsive force is negligible in comparison with that of the long-range attractive force. The former force comes into play only when the molecule is displaced towards the circumference of its space.

For a few substances μ and m can be calculated from the gaseous second virial coefficient by the method of Lennard-Jones (See Part II, p. 108). For normal organic liquids, $m = 11$, and μ can be related to the parachor P, which can be calculated from the atomic values without any direct measurement (See Part II, p. 107). Initially we will show how a number of properties of a liquid can be quantitatively deduced from T, σ and μ and m, or P, and we will then indicate how σ could be calculated from a knowledge of T, μ, λ, m and n.

3. *Surface Tension.*

Edser (*loc. cit.*, p. 62) has shown that the surface tension of a liquid is given by

$$\gamma = \frac{\pi\mu N^2}{8(m-5)V^2\sigma^{m-5}} \quad .. \quad .. \quad .. \quad .. \quad (3)$$

It should be noted that in deriving γ, the average effect of a molecule over a reasonably long time interval is obtained by assuming that its mean position is the centre of its spherical space, and that its vibrations can here be neglected.

Inserting (1) in (3) we have

$$\gamma = \frac{\pi\mu}{4(m-5)\sigma^{m+1}} \quad .. \quad .. \quad .. \quad .. \quad (4)$$

in which all the quantities are known.
Alternatively we can combine (1) and (3) to give

$$\gamma = \frac{\pi\mu}{4(m-5)} \frac{N^{\frac{m+1}{3}}}{V^{\frac{m+1}{3}} 2^{\frac{m+1}{6}}} \quad .. \quad .. \quad .. \quad (5)$$

$$= P^{\frac{m+1}{3}} \Big/ V^{\frac{m+1}{3}} \quad .. \quad .. \quad .. \quad .. \quad (6)$$

where

$$P^{\frac{m+1}{3}} = \frac{\pi\mu}{4(m-5)} \frac{N^{\frac{m+1}{3}}}{2^{\frac{m+1}{6}}} \quad .. \quad .. \quad .. \quad (7)$$

If we put $m = 11$, (6) becomes

$$\gamma = \frac{P^4}{V^4} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (8)$$

where

$$P^4 = \frac{\pi\mu N^4}{96} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (9)$$

that is

$$\mu = \frac{96\ P^4}{\pi N^4} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (10)$$

(8) is the parachor law for low vapour pressures. Since the parachor for normal liquids can be calculated from the molecular structure, (10) enables us to calculate μ for such liquids.

Table I gives values of μ and m for some liquefied gases calculated from the second virial coefficient (Part II, p. 108), and also values of μ for some

TABLE I.

Substance	m	μ	Substance	P*	$\mu \times 10^{85}$ (10)
He ..	7	$5{\cdot}77\times10^{-60}$	$(C_2H_5)_2O$	210·2	4·43
H_2 ..	8	$2{\cdot}33\times10^{-66}$	$(CH_3)_2CO$	160·2	1·49
Ne ..	7	$2{\cdot}55\times10^{-59}$	C_6H_{14} (*n*)	268·2	11·7
Ar ..	8	$1{\cdot}41\times10^{-65}$	$CHCl_3$	184·8	2·64
N_2 ..	8	$2{\cdot}02\times10^{-65}$	CCl_4	222·0	5·52
			C_6H_6	207·1	4·16

* Calculated from molecular structure.

normal organic liquids calculated by means of (10) (Part II, p. 107). These values are used throughout this paper. Table II shows the application

TABLE II.

Substance	T	$\sigma \times 10^8$	$\gamma_{(4)}$	$\gamma_{(obs.)}$
He ..	1·5	4·02	0·33	0·35
H_2 ..	15·0	3·97	2·5	2·8
Ne ..	24·7	3·38	5·9	5·6
Ar ..	85·0	4·03	13·2	13·2
N_2 ..	70·0	4·28	10·9	10·5

of (4) to those substances for which μ and m have been calculated from the second virial coefficient (Part II, p. 110); (8) is already known to hold with fair accuracy for normal liquids at temperatures of low vapour pressure.

4. *Internal Thermal Pressure.*

In Part III (p. 798), the thermal pressure on a unit plane in the liquid, which is the product of the number of molecular spaces in contact with the plane, the frequency of vibration of the corresponding molecules (see section 7) and the change in momentum in each vibration towards the plane due to the repulsive forces, is shown to be given by the equation,

$$p_T = \frac{2}{\sqrt{3}} \cdot \frac{k'T}{\beta\sigma^3} \quad .. \quad .. \quad .. \quad .. \quad (11)$$

where β is the fractional amplitude of vibration.

5. *Cohesive Pressure.*

Edser (*loc. cit.*, p. 58) has shown that the cohesive pressure K of a liquid is given by

$$K = \frac{2\pi\mu N^2}{3(m-4)\sigma^{m-4}V^2} \quad .. \quad .. \quad .. \quad .. \quad (12)$$

the terms due to the repulsive force being neglected. Substituting (1) in (12) we have

$$K = \frac{4\pi\mu}{3(m-4)\sigma^{m+2}} \quad .. \quad .. \quad .. \quad .. \quad (13)$$

in which all the quantities are known.

Inserting (10) and (1) in (12) and putting $m = 11$, we obtain

$$K = \frac{32}{7\sigma} \cdot \frac{P^4}{V^4} \quad .. \quad .. \quad .. \quad .. \quad (14)$$

The quantities in (13) and (14) are all known, V being at once derived from σ by means of (1). Table III shows the application of (13) and (14). The values obtained with (14) are of the same order as those deduced by other methods. (See Hildebrand, *Solubility*, 1924, p. 99).

TABLE III.

Substance	T	$\sigma \times 10^8$	K ats. (13)	Substance	T	$\sigma \times 10^8$	K ats. (14)
He ..	1·0	4·02	29	$(C_2H_5)_2O$	273	6·16	1415
H_2 ..	13·9	3·92	280	$(CH_3)_2CO$	293	5·55	1840
Ne ..	24·5	3·35	660	$C_6H_{14}(n)$	273	6·64	1350
Ar ..	83·1	4·02	1320	$CHCl_3$	288	5·71	2250
N_2 ..	63·1	4·23	1140	CCl_4	273	6·02	2300
				C_6H_6	279	5·87	2410

6. Fractional Amplitude of Vibration.

At equilibrium the thermal and cohesive pressures are equal, since the external pressure can be neglected in comparison ; equating (11) and (13) we have

$$\beta = \frac{\sqrt{3}(m-4)\sigma^{m-1}k\mathrm{T}}{2\pi\mu} \quad .. \quad .. \quad .. \quad (15)$$

or with (1) and (10), putting $m = 11$,

$$\beta = \frac{7\sqrt{3}k\mathrm{T}}{48\sigma^2} \cdot \frac{\mathrm{V}^4}{\mathrm{P}^4} \quad .. \quad .. \quad .. \quad .. \quad (16)$$

β can be calculated from (15) and (16). Further, differentiation of (15) with respect to T gives

$$\frac{d\beta}{d\mathrm{T}} = \frac{\beta}{\mathrm{T}} + \frac{(m-1)\beta}{\sigma}\frac{d\sigma}{d\mathrm{T}} \quad .. \quad .. \quad .. \quad (17)$$

$$= \frac{\beta}{\mathrm{T}} + \frac{(m-1)\beta\alpha}{3} \quad .. \quad .. \quad .. \quad (18)$$

As σ is assumed to be known at each temperature, α is known and hence from (18), $\frac{d\beta}{d\mathrm{T}}$ can be calculated, when β has been determined. Table IV shows the application of (15) and (16) to calculate β (*Cf.* Tables 1 and 2, Part III). The values are of the same order as those obtained for $\beta_{m.p.}$ in solids from specific heat and other data. Values for $\frac{d\beta}{d\mathrm{T}}$ are also given ; it is usually about two-thirds of α.

TABLE IV.

Substance	T	$\sigma\times10^8$	α	β (15)	$\frac{d\beta}{d\Gamma}$ (18)	Substance	T	$\sigma\times10^8$	α	β (16)	$\frac{d\beta}{d\Gamma}$ (18)
He	1·0	4·02	..	0·083	0·083	$(C_2H_5)_2O$	273	6·16	0·0015	0·128	0·0011
H_2	13·9	3·92	0·012	0·128	0·012	$(CH_3)_2CO$	293	5·55	0·0014	0·145	0·0012
Ne	24·5	3·35	0·014	0·153	0·011	$C_6H_{14}(n)$	273	6·64	0·0014	0·106	0·0009
Ar	83·1	4·02	0·0044	0·151	0·0034	$CHCl_3$ ..	288	5·71	0·0012	0·107	0·0008
N_2	63·1	4·23	0·0048	0·114	0·0031	CCl_4 ..	273	6·02	0·0012	0·085	0·0007
						C_6H_6 ..	279	5·87	0·0012	0·088	0·0007

7. *Frequency of Vibration.*

As shown in Part III (p. 797), the frequency of vibration of a molecule within its spherical space is given by

$$\nu = \frac{1}{\sqrt{2\pi}}\sqrt{\frac{kT}{m}}\frac{1}{\beta\sigma} \quad .. \quad .. \quad .. \quad .. \quad (19)$$

which with (15) gives

$$\nu = \frac{(\sqrt{2\pi})\mu}{\sqrt{3}(m-4)\sigma^m\sqrt{m}\sqrt{kT}} \quad .. \quad .. \quad .. \quad (20)$$

in which all the quantities are known. If we put $m = 11$, (20) on insertion of (1) and (10) gives

$$\nu = \frac{8\sqrt{6}}{7\sqrt{\pi}}\frac{P^4}{V^4}\frac{\sigma}{\sqrt{mkT}} \quad .. \quad .. \quad .. \quad (21)$$

Table V shows the application of (20) and (21). It should be noted that if in (19) we put $\beta = 0{\cdot}1$, the equation reduces to Lindemann's equation for the frequency at the melting-point (See Part III, p. 798).

TABLE V.

Substance	T	$\sigma\times10^8$	ν (20)	Substance	T	$\sigma\times10^8$	ν (21)
He ..	1·0	4·02	$5{\cdot}44\times10^{11}$	$(C_2H_5)_2O$ ..	273	6·16	$8{\cdot}84\times10^{11}$
H_2 ..	13·9	3·92	$1{\cdot}92\times10^{12}$	$(CH_3)_2CO$ ..	293	5·55	$1{\cdot}01\times10^{12}$
Ne ..	24·5	3·35	$7{\cdot}81\times10^{11}$	$C_6H_{14}(n)$ ..	273	6·64	$9{\cdot}06\times10^{11}$
Ar ..	83·1	4·02	$8{\cdot}64\times10^{11}$	$CHCl_3$ ..	288	5·71	$9{\cdot}21\times10^{11}$
N_2 ..	63·1	4·23	$1{\cdot}13\times10^{12}$	CCl_4 ..	273	6·02	$9{\cdot}45\times10^{11}$
				C_6H_6 ..	279	5·87	$1{\cdot}32\times10^{12}$

8. Viscosity.

In Part III (p. 802), it has been shown that

$$\eta = \frac{8R^{\frac{1}{2}}}{3\sqrt{\pi}N}\frac{M^{\frac{1}{2}}T^{\frac{1}{2}}}{\beta\sigma^2} \quad .. \quad .. \quad .. \quad .. \quad (22)$$

which with (15) gives

$$\eta = \frac{16\sqrt{\pi}}{3\sqrt{3}(m-4)}\frac{\mu}{\sigma^{m+1}}\frac{M^{\frac{1}{2}}}{R^{\frac{1}{2}}T^{\frac{1}{2}}} \quad .. \quad .. \quad .. \quad (23)$$

Putting $m = 11$, and inserting (1) and (10), (23) becomes

$$\eta = \frac{128}{7\sqrt{3\pi}}\frac{M^{\frac{1}{2}}}{R^{\frac{1}{2}}T^{\frac{1}{2}}}\frac{P^4}{V^4} \quad .. \quad .. \quad .. \quad .. \quad (24)$$

Table VI shows the application of (23) and (24). For substances for which η is known, the agreement is fair, particularly when allowance is made for the fact that for some of the substances, data near the melting-point are not available.

TABLE VI.

Substance	T	$\sigma\times10^8$	$\eta_{(23)}$	η (obs.)	Substance	T	V	$\eta_{(24)}$	η (obs.)
He ..	2·3	4·02	0·0002	0·0003	$(C_2H_5)_2O$ ..	198	90·7	0·011	0·009
H_2 ..	13·9	3·92	0·0006	..	$(CH_3)_2CO$ ..	200	64·9	0·013	0·013
Ne ..	24·5	3·35	0·0029	..	C_6H_{14} (*n*) ..	273	127·0	0·007	0·004
Ar ..	83·1	4·02	0·0053	..	$CHCl_3$ ..	263	77·2	0·014	0·008
N_2 ..	63·1	4·23	0·0046	..	CCl_4 ..	273	94·2	0·015	0·013
					C_6H_6 ..	279	87·3	0·011	0·008

9. Internal Work of Evaporation.

Edser[3] has shown that the internal work of evaporation is given by the formula

$$A_i = \frac{2\pi\mu N^2}{3(m-4)V\sigma^{m-4}} \quad .. \quad .. \quad .. \quad .. \quad (25)$$

which inserting (1) gives,

$$A_i = \frac{2\sqrt{2}\pi\mu N}{3(m-4)\sigma^{m-1}} \quad .. \quad .. \quad .. \quad .. \quad (26)$$

(26), when m is put $= 11$, becomes, if (1) and (10) be inserted,

$$A_i = \frac{32}{7\sigma}\frac{P^4}{V^3} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (27)$$

[3] *Loc. cit.*, p. 67.

10. Internal Latent Heat of Evaporation.

The Gibbs-Helmholtz equation gives

$$L_i = A_i - T\left(\frac{\delta A_i}{\delta T}\right)_V \quad .. \quad .. \quad .. \quad .. \quad (28)$$

From (25) we have

$$\left(\frac{\delta A_i}{\delta T}\right)_V = \frac{-(m-4)A_i}{\sigma}\left(\frac{\delta \sigma}{\delta T}\right)_V \quad .. \quad .. \quad .. \quad (29)$$

which with the assumption contained in (2) gives

$$\left(\frac{\delta A_i}{\delta T}\right)_V = \frac{-(m-4)A_i}{\sigma}\left(\frac{\delta \sigma}{\delta T}\right)_p \quad .. \quad .. \quad .. \quad (30)$$

$$= \frac{-(m-4)A_i\alpha}{3} \quad .. \quad .. \quad .. \quad (31)$$

since

$$\alpha = \frac{1}{V}\left(\frac{\delta V}{\delta T}\right)_p \quad .. \quad .. \quad .. \quad .. \quad (32)$$

and hence from (1)

$$= \frac{3}{\sigma}\left(\frac{\delta \sigma}{\delta T}\right)_p \quad .. \quad .. \quad .. \quad .. \quad (33)$$

Hence from (28) and (31),

$$L_i = A_i\left[1 + \frac{T(m-4)\alpha}{3}\right] \quad .. \quad .. \quad .. \quad (34)$$

where A_i is given by (26). From (27) we have

$$L_i = \frac{32}{7\sigma}\frac{P^4}{V^3}\left[1 + \frac{7T\alpha}{3}\right] \quad .. \quad .. \quad .. \quad (35)$$

Table VII shows the application of (34) and (35). The agreement with (34) is better than with (35).

11. Specific Heat Equations.

In Part I (p. 528), the application of the following three specific heat equations is discussed :—

$$(a)\ C_{pl} - C_{vg} = -\left(\frac{\delta L_i}{\delta T}\right)_p \quad .. \quad .. \quad .. \quad .. \quad (36)$$

$$= A_i\alpha\left[1 + \frac{T(m-1)(m-4)\alpha}{9}\right] \quad .. \quad .. \quad (37)$$

$$(b)\ C_{pl} - C_{vl} = -\left(\frac{\delta L_i}{\delta V}\right)_T\left(\frac{\delta V}{\delta T}\right)_p \quad .. \quad .. \quad .. \quad (38)$$

$$= -\left(\frac{\delta L_i}{\delta V}\right)_T \alpha V \quad .. \quad .. \quad .. \quad .. \quad (39)$$

$$= L_i\alpha\ ^4 \quad .. \quad .. \quad .. \quad .. \quad (40)$$

$$= A_i\alpha\left(1 + \frac{(m-4)\alpha T}{3}\right) \quad .. \quad .. \quad .. \quad (41)$$

[4] *Cf.* Tyrer, *Zeit. Phys. Chem.*, 1914, **87**, 177.

TABLE VII.

Substance	T	$\sigma\times10^8$	a	A_i cals. (26)	L_i cals. (34)	L_i cals. (obs.)	Substance	T	$\sigma\times10^8$	a	A_i K-cals. (27)	L_i K-cals. (35)	L_i K-cals. (obs.)
He ..	1·75	4·02	..	19	19	19	$(C_2H_5)_2O$ ..	273	6·16	0·0015	3·43	6·72	6·28
H_2 ..	15·0	3·97	0·012	162	201	189	$(CH_3)_2CO$ ..	293	5·55	0·0014	3·27	6·40	7·06
Ar ..	87·1	4·05	0·0046	845	1300	1326	$C_6H_{14}(n)$ ..	273	6·64	0·0014	4·15	7·82	7·11
N_2 ..	63·1	4·23	0·0048	891	1250	1330	$CHCl_3$ ..	288	5·71	0·0012	4·33	7·87	6·98
							CCl_4 ..	273	6·02	0·0012	5·24	9·26	7·45
							C_6H_6 ..	279	5·87	0·0012	5·09	9·07	7·71

TABLE VIII.

Substance	T	V	a	L_i ergs. (34)	c (44)	Substance	T	V	a	L_i ergs. (35)	c (44)	c (obs.)
H_2 ..	15·0	26·3	0·012	$8·43\times10^9$	$5·61\times10^{-10}$	$(C_2H_5)_2O$	273	100·5	0·0015	$2·81\times10^{11}$	$14·7\times10^{-11}$	$15·0\times10^{-11}$
Ar ..	87·1	28·5	0·0046	$5·45\times10^{10}$	$2·10\times10^{-10}$	$(CH_3)_2CO$	293	73·3	0·0014	$2·68\times10^{11}$	$11·3\times10^{-11}$	$12·4\times10^{-11}$
N_2 ..	63·1	32·0	0·0048	$5·24\times10^{10}$	$1·85\times10^{-10}$	$C_6H_{14}(n)$	273	127·0	0·0014	$3·28\times10^{11}$	$14·8\times10^{-11}$	$12·5\times10^{-11}$
						$CHCl_3$ ..	288	79·8	0·0012	$3·30\times10^{11}$	$8·4\times10^{-11}$	$9·7\times10^{-11}$
						CCl_4 ..	273	94·2	0·0012	$3·88\times10^{11}$	$7·9\times10^{-11}$	$9·0\times10^{-11}$
						C_6H_6 ..	279	87·3	0·0012	$3·80\times10^{11}$	$7·7\times10^{-11}$	$8·2\times10^{-11}$

$$(c)\ C_{vl} - C_{vg} = -\left(\frac{\delta L_i}{\delta T}\right)_V \quad .. \quad .. \quad .. \quad .. \quad (42)$$

$$= \frac{A_i a^2 T(m-4)^2}{9} \quad .. \quad .. \quad .. \quad .. \quad (43)$$

As Tables II and III (Part I) show, the agreement with m, 9 to 11 between the observed and calculated values is moderately good, particularly when it is remembered that the fundamental equations, (36), (38) and (42) are only approximately valid. In these calculations (4) was used to replace μ by γ.

12. *Compressibility.*

The compressibility of a normal liquid[5] is given by

$$c = \frac{TaV}{L_i} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (44)$$

Table VIII shows values of c calculated from (44) using values of L_i derived from (34) or (35). For those substances for which c has been measured, the agreement between the calculated and observed values is satisfactory.

13. *Vapour Pressure.*

A vapour-pressure equation has also been derived (Part III, p. 803) but the results obtained are only approximate and it need not further be discussed here.

14. *Direct Calculation of* σ.

As shown in Part IV, the total work done by the repulsive and attractive forces as a molecule passes from the centre of its spherical space to a distance x from that centre is given by

$$\overline{W}_1 = 4\sqrt{2}\pi\left(\frac{\mu\overline{m}}{(m-1)\sigma^{m-1}} - \frac{\lambda\overline{n}}{(n-1)\sigma^{n-1}}\right) \quad .. \quad .. \quad (45)$$

where

$$\overline{m} = \frac{X^{-(m-5)} - Y^{-(m-5)}}{2\left(\frac{x}{\sigma}\right)(m-5)\ (m-3)} + \frac{X^{-(m-4)} + Y^{-(m-4)}}{2(m-4)\ (m-3)} - \frac{1}{(m-4)} \quad .. \quad (46)$$

and $\overline{n}$ corresponds to $\overline{m}$.

In (46)

$$X = 1 - \frac{x}{\sigma} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (47)$$

and

$$Y = 1 + \frac{x}{\sigma} \quad .. \quad .. \quad .. \quad .. \quad (48)$$

The equilibrium equation is

$$\tfrac{1}{2}kT = -4\sqrt{2}\pi\left(\frac{\mu\overline{m}}{(m-1)\sigma^{m-1}} - \frac{\lambda\overline{n}}{(n-1)\sigma^{n-1}}\right) \quad .. \quad .. \quad (49)$$

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[5] *Cf.* Edser, *loc. cit.*, p. 80; Lewis, *Zeit. Phys. Chem.*, 1911, **78**, 24.

The value of $\frac{x}{\sigma}$ which satisfies this equation is $= \beta/2$.

From (15) we have

$$\sigma = C\,\beta^{\frac{1}{(m-1)}} \quad .. \quad .. \quad .. \quad .. \quad (50)$$

where C is a constant and insertion of (50) in (49), gives an equation in β which can be solved by graphical methods when μ, λ, m, n, and T are known.

The results given in the previous portion of this paper indicate that μ and m can be calculated from the second virial coefficient and applied to the liquid state. Attempts to use the corresponding values of λ and n in (49) led to values of β which were much too large. The repulsive force though negligible when the molecule is at the centre of its spherical space appears to increase when the molecule is displaced from the centre of the space much more rapidly than the corresponding repulsive force in the gaseous state. Until some means have been found for determining λ and n for the liquid state, it will be impossible to evaluate (49) and thus directly determine β and thence σ by means of (15).

NOTATION ADOPTED.

A_i	Internal work of evaporation. Work done against van der Waals forces in evaporating isothermally 1 g.-mol. of a liquid to the state of infinitely dilute vapour.
c	Compressibility.
C_{pl}	Molecular heat of the liquid at constant pressure.
C_{vl}	Molecular heat of the liquid at constant volume.
C_{vg}	Molecular heat of the liquid vapour at constant volume.
K	Internal pressure.
k	Boltzmann's constant.
L_i	Internal latent heat of vapourisation.
m	Index of the power of the inverse distance expressing the variation of the attractive force between two molecules.
M	Molecular weight.
m	Mass of a molecule. See also (46).
n	Index for the repulsive force.
N	Number of molecules in 1 g.-mol.
P	Parachor constant.
p	External pressure.
p_T	Internal thermal pressure.
R	Gas constant.
r	Distance between two molecules.
T	Absolute temperature.
V	Volume of 1 g.-mol. of the liquid in the normal state at T.
x	Distance a molecule is removed from the centre of its spherical space.
α	Coefficient of thermal expansion of a liquid.
β	Fractional amplitude of vibration of a molecular centre within its spherical space.
η	Viscosity.
γ	Surface tension.
λ	Repulsive force coefficient.
μ	Attractive force coefficient.
ν	Frequency of vibration.
σ	Diameter of spherical space which a molecule keeps clear around it by its thermal motion.

RAMAN SPECTRUM OF DEUTERIUM: II.

Intensity and Polarisation Characters.

By S. Bhagavantam.
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Received October 24, 1935.

1. *Introduction.*

In Part I of this series (Bhagavantam, 1935), the author described a preliminary investigation of the Raman spectrum of deuterium. In the present paper a quantitative study of the intensity and polarisation characters of the various Raman lines is made and the results are compared with the conclusions of the existing theories of Raman scattering by gaseous molecules (Manneback, 1930 and Placzek, 1934). More intense and satisfactory photographs of the scattered light have incidentally been obtained and a complete analysis is made of all the new lines appearing in the scattered spectra.

2. *Experimental.*

Measurement of Relative Intensities.—The preparation of deuterium under pressure, the experimental tube and the illuminating arrangements, have all been already described in earlier papers. In this investigation an intense picture is obtained by giving a continuous exposure of about 6 days for purposes of measuring the relative intensities of the lines. The Plate is run through a Moll microphotometer and the densities of the various lines are obtained in the usual way. A set of intensity marks is recorded on the same Plate by the method of varying slit widths using the continuous radiation emitted by a standard quartz globe tungsten ribbon lamp as the source. A steady current of 14·8 amperes is maintained in the lamp by feeding it from a battery of 220 volts. The colour temperature T of the lamp corresponding to this current is given by the makers as 2660 and the radiation emitted by the lamp is therefore assumed to obey the Wien's law $I\lambda = A\lambda^{-5}\, e^{-c_2/T\lambda}$ where $c_2 = 1{\cdot}432$, $T = 2660$ and A is a constant. The density at any desired wave-length is obtained for each of the intensity marks by running the Plate through the microphotometer under the same conditions as above and the corresponding intensities are taken as proportional to their respective slit widths. In this way, the density-log intensity curves are drawn for each wave-length at which the various Raman lines that are to be compared with each other appear. The intensity of any line as a fraction

of the standard radiation having the same wave-length as the line itself is easily read off from the above curves and the relative intensities of the various lines are then computed from a knowledge of the intensity distribution in the radiation emitted by the lamp. It may easily be seen that this procedure totally eliminates errors due to variations in the photographic sensitivity of the Plate in different regions of the spectrum.

Polarisation Characters.—For this purpose, a suitably oriented double image prism is introduced in the path of the scattered light and the two images representing respectively the vertical and the horizontal components are focussed one above the other on the slit of the spectrograph. They are thus simultaneously photographed (see Plate XXV) and fluctuations in the intensity of the incident radiation are not therefore of any consequence. On the same Plate is recorded as before a set of intensity marks by the method of varying slit widths using the standard tungsten ribbon lamp. Density–log intensity curves are drawn for each one of the wave-lengths at which the Raman lines appear and a knowledge of the densities of the horizontal and vertical components of any particular line enables us to obtain the depolarisation ratio from the corresponding density–log intensity curve. Depolarisation factors obtained in this manner are subject to corrections arising from (i) depolarisation introduced by oblique refraction at the prism surfaces, and (ii) a certain lack of transversality between the incident and scattered rays. The method of determining and applying these corrections has already been described by the author in earlier papers (Bhagavantam, 1932) and the values given in the following pages are obtained after applying these corrections.

3. *The Raman Spectrum of Deuterium.*

The main frequency shifts observed in the Raman spectrum of deuterium have already been given in Part I. In a subsequent paper (Bhagavantam, 1935), a further set of faint lines have been reported and attributed to the presence of a small proportion of hydrogen deuteride molecules in the sample under investigation. The relation of the observed frequency shifts to the molecular constants has been discussed. In more intense pictures that have since been obtained, all these frequencies are confirmed and some of them are found to be excited by two or even three different lines of the incident spectrum. It may be noted that using the full range of the mercury lamp in the visible region, no fewer than about 28 lines have been recorded with this simple substance. A complete list of the observed lines and their assignments to the various exciting radiations are given below in Table I.

TABLE I. *Raman Spectrum of Deuterium.**

Wave-length	Approx. Rel. intensity	Exciting line	Quantum transition	
			J	n
3979·4	1	4046	4 → 2	
3999·1	1	,,	3 → 1	
4017·9	2	,,	2 → 0	
4090·0*	0	,,	0 → 2	
4096·3	4	,,	1 → 3	
4097·8	1	3650	..	0 → 1
4104·5	1	3654	..	0 → 1
4115·7	5	4046	2 → 4	
4121·5*	½	,,	1 → 3	
4128·0	½	4077	1 → 3	
4135·1	2	4046	3 → 5	
4147·6	½	4077	2 → 4	
4154·9	2	4046	4 → 6	
4281·3	1	4358	4 → 2	
4302·5	1	,,	3 → 1	
4308·7*	0	,,	2 → 0	
4324·5	2	,,	2 → 0	
4392·7	4	,,	0 → 2	
4409·6*	0	,,	0 → 2	
4415·6	3	,,	1 → 3	
4438·7	5	,,	2 → 4	
4443·8*	½	,,	1 → 3	
4461·6	2	,,	3 → 5	
4478·9*	0	,,	2 → 4	
4484·1	2	,,	4 → 6	
4604·3	4	4046	..	0 → 1
4644·7	½	4077	..	0 → 1
5009·5	0	4358	..	0 → 1

* Lines marked with an asterisk arise from hydrogen deuteride molecules.

4. Relative Intensities of the Rotation Lines.

In Table II the observed intensities of the various rotation lines are compared with the calculated values. The calculations, details of which are to be found in Part I, refer to a temperature of 30° C. The figures are only relative and have no absolute significance.

TABLE II.

Relative Intensities of the Rotation Lines.

Transition	PP Series		Transition	RR Series	
	Calculated	Observed		Calculated	Observed
2 → 0	0·57	0·69	0 → 2	1·33	1·34
3 → 1	0·22	0·4	1 → 3	0·90	0·82
4 → 2	0·20	0·4	2 → 4	1·47	1·40
5 → 3	0·01	..	3 → 5	0·41	0·46
			4 → 6	0·32	0·38
			5 → 7	0·02	..

The agreement between the two sets of values is fairly satisfactory. Appreciable discrepancies are, however, to be noticed in connection with the two relatively faint antistokes lines but these may be attributed to the fact that errors in photometric measurements are more likely in cases of such faint lines. According to the theory we should expect the 2→4 line to be the most intense and this is confirmed. The calculations clearly show that the intensity of the rotation lines rapidly falls off from the sixth line onwards on the stokes side and the fourth line onwards on the antistokes side and in order to obtain these, one would have had to expose the picture for about fifteen times the normal period. The non-appearance of these lines in the photographs (Plate XXV) is thus fully explained.

The fact that the rotation lines representing transitions between even levels are stronger than those representing transitions between odd levels is contrary to what is observed in ordinary hydrogen and shows that the nuclei obey Bose-Einstein statistics. The quantitative agreement between the observed results and the detailed calculations as given in Part I further confirms the view that the deuterium nucleus has a spin moment of one unit. The deuterium nucleus thus differs from the hydrogen nucleus in these two

important respects as the latter conforms to Fermi-Dirac statistics and has a spin moment of only half a unit.

5. Polarisation of the Raman Lines in Deuterium.

The Raman spectrum obtained for this purpose with a double image prism in the path of the scattered light is reproduced in the Plate accompanying this paper. The vertical and horizontal components are clearly separated from each other. The almost complete depolarisation of all the rotation lines stands out in marked contrast with the nearly perfect state of polarisation of the three vibration lines marked V. R. and excited respectively by λ 3654, 4046 and 4358 radiations of the mercury arc. The vibration line excited by λ 3650 falls nearly on the top of a rotation line 1→3 and the admixture consequently exhibits a state of polarisation which is intermediate. The results obtained are given in Table III.

TABLE III.

Depolarisation of the Raman Lines.

Transition	J : 2→0	0→2	1→3	2→4	3→5	n : 0→1 J : 0→0, 1→1, etc.
Depolarisation	0·84	0·86	0·84	0·84 0·88	0·83	0·18

All the values, with the exception of 0·88 for 2→4 rotation transition and 0·18 for the vibration transition, refer to lines excited by λ 4358. The latter two are obtained with lines excited by λ 4046. A depolarisation factor of 0·86 is to be expected for all rotation lines when unpolarised incident light is used and the observed results closely agree with this expectation. The low value of 0·18 for the vibration line compares well with 0·13 reported earlier by the author for the vibration line in ordinary hydrogen (Bhagavantam, 1932).

6. Intensity of the Vibration Line.

A direct comparison is made of the intensity of the vibration line excited by λ 4046 with the rotation line 2→4 excited by the same radiation. Since this rotation line has been found to be about 1·4/5·9 of the total rotational scattering (see Table II), it is easy to compute the intensity of the vibration scattering in relation to the aggregate rotational scattering. These figures are given in Table IV. If we further provisionally assume that the aggregate depolarisation of the scattered light in deuterium is the same as in hydrogen (about 2%), it follows that the aggregate rotational

scattering will be about 3/100 of the Rayleigh scattering and an approximate estimate may be made of the intensity of the vibration scattering in relation to that of the Rayleigh line. The figure so obtained is given in column 4 of Table IV. This may be compared with the corresponding figure $4 \cdot 2 \times 10^{-3}$

TABLE IV.

Intensity of the Vibration Line.

Comparison	Vibration line (n · 0→1) / Rotation line (J: 2→4)	Vibration line (n: 0→1) / Aggregate rotation scattering	Vibration line (n: 0→1) / Rayleigh line
Relative Intensity	0·43	0·10	3×10^{-3}

obtained in ordinary hydrogen and shows that like hydrogen, the vibration Raman line in deuterium is about 1/300 of the Rayleigh line. Such a large intensity of the vibration scattering is exceptional in gases and has so far been observed only in hydrogen besides deuterium.

7. *Summary and Conclusion.*

Measurements have been made of the intensity and polarisation of the lines in the Raman spectrum of deuterium. The results, when compared with those calculated from the theory of rotational Raman scattering due to Manneback, show satisfactory agreement.

The vibration Raman line in deuterium is found to exhibit a depolarisation factor of 0·18 and an intensity of about one-tenth the aggregate intensity of the rotational scattering. From this result it is estimated that the intensity of the vibration line is about 1/300 of that of the Rayleigh line. This is an unusually large ratio for gases and has hitherto been found only in hydrogen.

Further work in relation to the fine structure of the vibration line and the inter-comparison of the P, Q and R branches is in progress and will form the subject-matter of the next paper in this series.

The author desires to express his grateful thanks to Prof. Sir C. V. Raman for his kind interest in the work.

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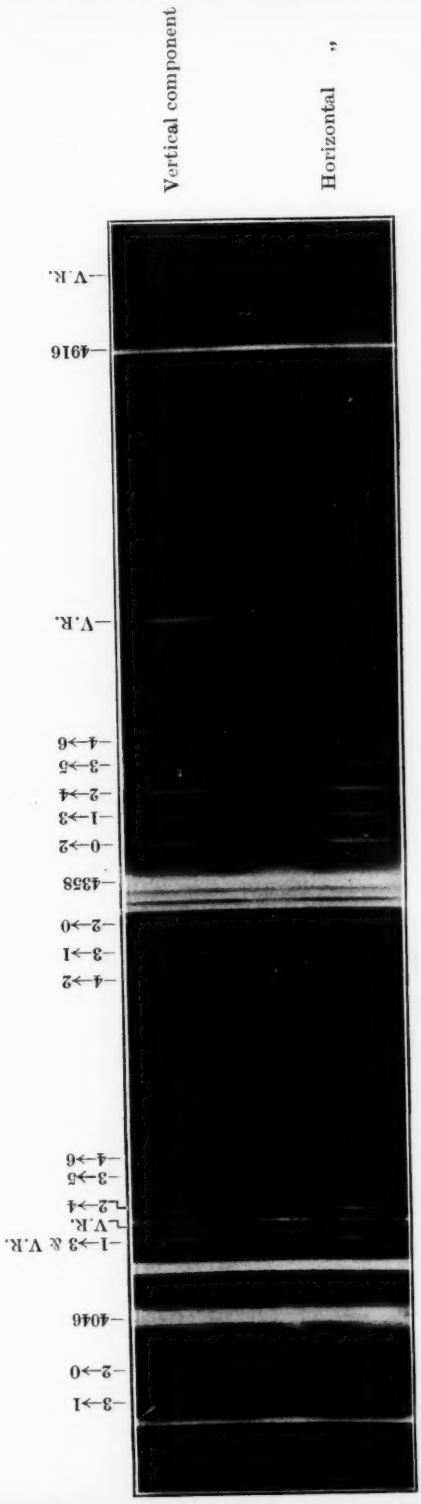

Raman Spectrum of Deuterium taken with a double image prism in the path of the scattered beam to show the state of polarisation of the various lines.

A STUDY OF THE BENZOIN REACTION—IV.

The Kinetics of the Benzoin Reaction in the Presence of Organic Solvents.

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Introduction.

For some time past this laboratory has been engaged on a study of the kinetics of the benzoin reaction between solid potassium cyanide and benzaldehyde.[1] It has been shown that when pure potassium cyanide and pure benzaldehyde react, two concurrent reactions take place : a fast homogeneous autocatalytic reaction, which requires the presence of benzoin, between benzaldehyde and the trace of potassium cyanide dissolved in it ; and a slow heterogeneous reaction between benzaldehyde and the solid potassium cyanide.

The object of the present paper has been to study the reaction between potassium cyanide and benzaldehyde in the presence of inert organic liquids and of hydroxy-compounds.

It has been shown that with inert solvents the heterogeneous reaction is unaffected, but the homogeneous reaction is decelerated ; because, a portion of the dissolved potassium cyanide is precipitated. The action of hydroxy-compounds is complicated, but on the whole, they accelerate the reaction.

Morton and Stevens[2] have previously investigated at room temperatures the course of the reaction in presence of relatively large amounts of various solvents, but owing to the difference between their experimental conditions and ours it is difficult to compare the results.

Materials Employed.

Benzaldehyde.—Merck's purest benzaldehyde, which gave consistent results, was used. It was stored in small quantities in an atmosphere of nitrogen and checked at intervals by standard experiments.

Potassium cyanide.—Kahlbaum's purest cyanide, which had been dried at 110° C. at 2 mm. pressure for 2 hours, was used. It always gave consistent results indicating uniformity of particle size.

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[1] Parts I, II and III, *J. Phys. Chem.*, 1935, **39**, 727, 901, 907; *Curr. Sci.*, 1935, **4**, 94.

[2] *J.A.C.S.*, 1930, **52**, 2031.

Benzene.—Merck's purest thiophene-free benzene was used.

Chlorobenzene.—Merck's pure chlorobenzene, freshly distilled, was used. In a few control experiments Kahlbaum's purest chlorobenzene was found to give similar results.

Toluene.—Merck's purest toluene was used after distilling. Kahlbaum's toluene, "free from sulphur, for the determination of molecular wieghts", gave similar results.

Chlorotoluene.—Kahlbaum's chlorotoluenes (*o*-, *m*- and *p*-) were used after distilling.

Benzyl chloride.—Kahlbaum's purest benzyl chloride was used.

Cyclohexane.—Kahlbaum's cyclohexane was used after distilling.

Pentane.—Kahlbaum's purest pentane reagent was used.

Chloroform and Carbon tetrachloride.—Kahlbaum's purest varieties were employed.

Thiophene.—Kahlbaum's purest thiophene was used.

Acetone.—Kahlbaum's acetone " Pro Analysi" was employed; Kahlbaum's acetone "from bisulphite compound" gave similar results.

Alcohols.—Kahlbaum's " Methanol, Pro Analysi " was used; Merck's absolute alcohol was dehydrated over calcium metal and distilled before use. Kahlbaum's purest ethylene glycol and Merck's extra pure glycerol, freshly distilled under reduced pressure and kept in presence of phosphorous pentoxide, were also employed. Pure samples of erythrite, mannite, dulcite, sorbite and inosite from Kahlbaum were used.

Experimental Results.

Benzene.—Figs. 1, 2 and 3 show the effect of addition of benzene on the rate of the benzoin reaction. It will be seen that the curves obtained with the same quantity of benzene and different amounts of potassium cyanide, are parallel for the autocatalytic portion of the reaction, and that increase in the amount of benzene decreases the rate of reaction. Since the curves are parallel the rate of the autocatalytic reaction is seen to be, as in the experiments without benzene (*loc. cit.*, Part I, p. 733), independent of the total quantity of KCN present, and determined by the quantity of KCN dissolved in the benzene-benzaldehyde-benzoin mixture.

The equation for calculating the course of the reaction curve for the reaction upto the conversion of about half of the benzaldehyde, which was worked out in Part I, can here be applied using the same value for the heterogeneous constant as previously employed and choosing a smaller value

for the homogeneous constant, since a portion of the potassium cyanide has been precipitated. The equation is :—

$$t-c' = -1/k_1\left[\frac{-50}{(10+X')n'} + \frac{(11\cdot51)\ (30+2X')}{(10+X')^2}\log n' - \frac{(20+X')^2}{(10+X')^2}(1\cdot15)\log(10+X'-n')\right]$$

or, when X′ is small,

$$t-c' = -1/k_1[-5/n' + 3\cdot45\log n' - 4\cdot60\log(10+X'-n')],$$

where

n' =gram. benzaldehyde remaining at time t,
k_1 =the value of the homogeneous constant,
$X' = 2k_2'/k_1$, k_2' being the heterogeneous constant,
and c' is a constant.

k_2' for 1g. effective KCN per 10 g. benzaldehyde $=0\cdot185$, and k_1 is chosen so that the curve will fit one result. Effective KCN, it may be noted, is the gross quantity of potassium cyanide used less 0·17 g., since it has been found previously (Part I, p. 730) that 0·17 g. KCN is always ineffective in the experiments.

Other Inert Solvents.—The results with chlorobenzene, toluene, chlorotoluene, benzyl chloride, cyclohexane, pentane, chloroform and carbon tetrachloride were of the same type as with benzene. Pentane was found to have a definite inhibiting effect though Morton and Stevens (*loc. cit.*) claim that it accelerates the reaction.

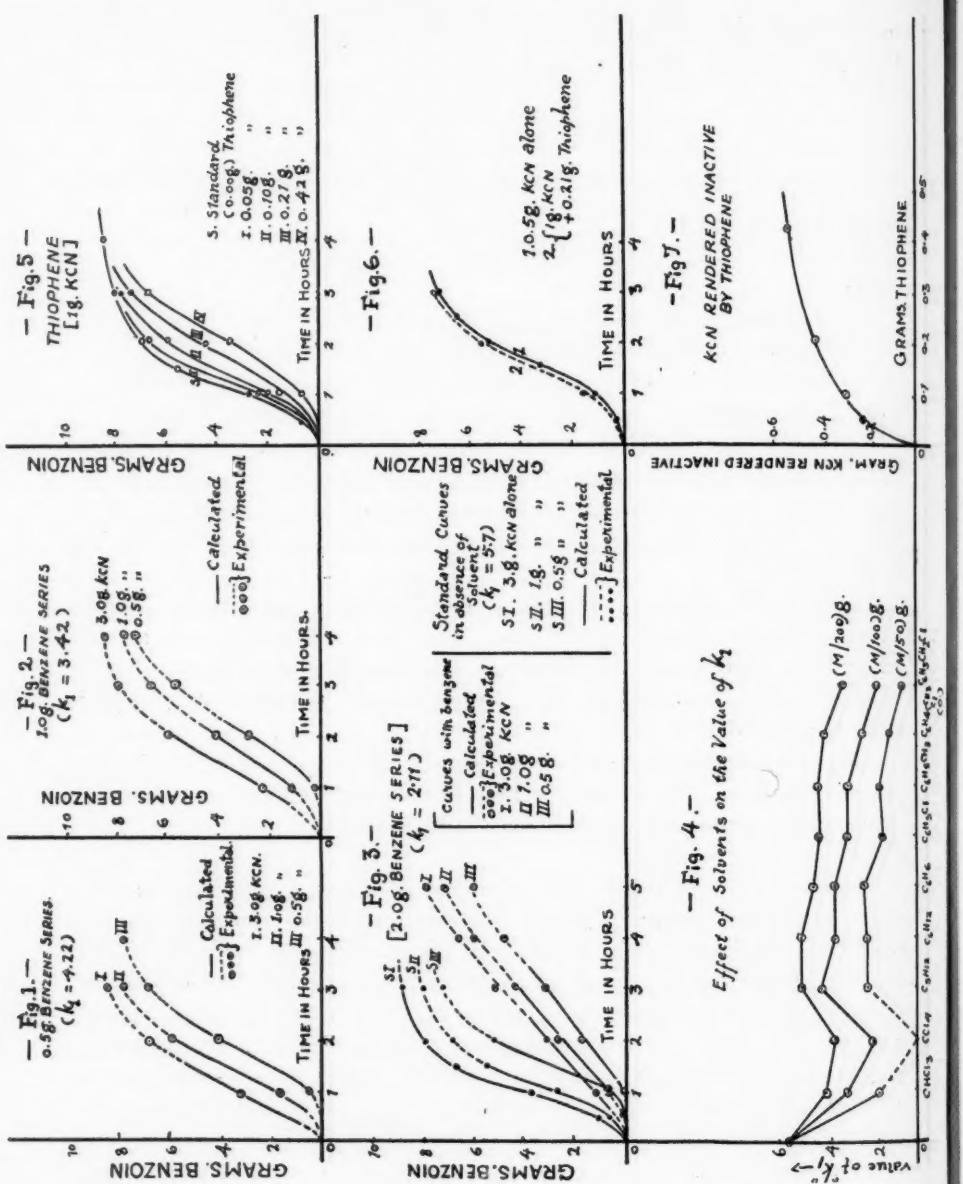
Fig. 4 shows the effect of various solvents on the value of k_1, the homogeneous constant. The action of carbon tetrachloride is greatest. Pentane, cyclohexane and benzene have much the same effect.

Thiophene.

Experiments were made with thiophene as it was found that benzene, not thiophene-free, showed a greater inhibiting action than the pure benzene employed. The results with thiophene show that it is an inhibitor of the type studied in Part II ; very small quantities prove definitely inhibiting.

Fig. 5 shows the effect of quantities of up to 0·42 g. on the reaction. Since it acts purely on the heterogeneous reaction and the homogeneous reaction is not affected, it is possible to obtain a coincidence between curves with a smaller amount of pure potassium cyanide and potassium cyanide in presence of thiophene. (See Fig. 6 ; *cf.* Part II, p. 901.)

For each of the thiophene curves we can find what was the equivalent amount of pure potassium cyanide that gives the same results, and in this way obtain Fig. 7 which shows the amount of potassium cyanide rendered


— Fig. 1. —
0.5g. BENZENE SERIES.
(k_1 = 4.22)
GRAMS. BENZOIN
TIME IN HOURS
Calculated
Experimental
I. 3.0g. KCN.
II. 1.0g. "
III 0.5g. "
— Fig. 2. —
1.0g. BENZENE SERIES
(k_1 = 3.42)
3.0g. KCN
1.0g. "
0.5g. "
Calculated
Experimental
— Fig. 3. —
[2.0g. BENZENE SERIES]
(k_1 = 2.11)
Curves with benzene
Calculated
Experimental
I. 3.0g. KCN
II 1.0g. "
III 0.5g. "
Standard Curves
in absence of
Solvent
(k_1 = 5.7)
SI. 3.0g. KCN alone
SII. 1g. " "
SIII. 0.5g. " "
Calculated
Experimental
— Fig. 4. —
Effect of Solvents on the Value of k_1
value of k_1
CHCl3 CCl4 C6H6 C6H5Cl C6H4Cl2 C6H3Cl3 C6H5NO2
— Fig. 5 —
THIOPHENE
[1g. KCN]
S. Standard.
(0.00g.) Thiophene
I. 0.05g. "
II. 0.10g. "
III. 0.27g. "
IV. 0.42g. "
— Fig. 6. —
1.0.5g. KCN alone
2. [1g. KCN
+0.21g. Thiophene
— Fig. 7. —
KCN RENDERED INACTIVE
BY THIOPHENE
GRAM. KCN RENDERED INACTIVE
GRAMS. THIOPHENE
(M/200)g.
(M/100)g.
(M/50)g.

inactive by given amounts of thiophene. It will be seen that the curve is of the adsorption type, the effect of small quantities of thiophene being much greater in proportion.

Acetone.

As benzoin accelerates the reaction, the effect of acetone was studied, and it was found that it also acted as an accelerator as shown in Figs. 8 and 9. The accelerated portions of the curves for the same quantity of acetone are parallel and can be reproduced by the equation :—

$$t-c' = -1/k_1[-5/n' + 3\cdot45 \log n' - 4\cdot60 \log (10+X'-n')]$$

by taking the normal value of k_2', the heterogeneous constant, and an increased value of k_1 which is independent of the amount of potassium cyanide present.

Acetone, therefore, would appear to act by increasing the amount of potassium cyanide dissolved in a given mixture of benzaldehyde and benzoin. Fig. 10 shows that the value of k_1 plotted against the amount of acetone gives a straight line.

Methyl and Ethyl Alcohols.

Both alcohols show an accelerating effect on the reaction. The results are, however, complicated (see Figs. 11 and 12). Small quantities accelerate the heterogeneous reaction; intermediate quantities delay the start of the homogeneous catalytic reaction, while larger amounts accelerate the reaction from the beginning.

Ethylene Glycol.

The results with ethylene glycol (Fig. 13) are of the same type as those obtained with methyl and ethyl alcohols.

Glycerol.

With different amounts of glycerol and the same quantity of KCN the time-yield curves are nearly parallel (see Fig. 14), showing that the rate of the accelerated reaction is independent of the quantity of glycerol used. Owing to the limited solubility of glycerol in benzaldehyde a constant amount of glycerol is dissolved in the benzaldehyde. Glycerol also accelerates the heterogeneous reaction.

Fig. 15 shows that the curves obtained with small quantities of alcohols can be made approximately to coincide with curves obtained in the absence of alcohol and with larger quantities of KCN. Thus we may deduce that alcohols in small quantities do not affect greatly the homogeneous catalytic reaction but accelerate the heterogeneous reaction.

Polyhydric Alcohols.

Polyhydric alcohols increase the rate of reaction even in small amounts

HYDROXY COMPOUNDS.
[1.0g. KCN]
- ACETONE -
- Fig.8. -
18 Acetone Series
(K_1 = 6·6)
Calculated
Experimental
I. 0.58 KCN
II. 1·08 "
GRAMS. BENZOIN
TIME IN HOURS
- Fig.9. -
1·08 KCN alone
0.58 " "
28 Acetone Series
(K_1 = 7·8)
Calculated
Experimental
I. 0.58. KCN
II. 1·08 KCN
GRAMS. BENZOIN
TIME IN HOURS
- Fig.10. -
Effect of Acetone on the Value of K_1
value of K_1
- Fig.11. -
METHYL ALCOHOL
S. Standard Curve (in absence of alcohol.)
I. 0.158 Alcohol
II. 0·66 "
III. 1·38 "
IV 1·58 "
GRAMS. BENZOIN
TIME IN HOURS
- Fig.12. ETHYL ALCOHOL
S. Standard
1. 0.28 Et. Alcohol
2. 1·38 "
3. 3·68 "
4. 5·08 "
5. 5·58 "
(S) BENZOIN
TIME IN HOURS
- Fig.13. ETHYLENE GLYCOL
S. Standard
I. 0.058 Glycol
II. 0.18 "
III. 0.28 "
IV. 0·38 "
GRAMS. BENZOIN
- Fig.14. -
GLYCEROL
S. Standard
I. 0.055g Glycerol
II. 0.07g. "
III. 0.14g. "
IV. 0.21g. "
GRAMS. BENZOIN
TIME IN HOURS
- Fig.15. -
3g. KCN alone
(Alcohol + 1g. KCN)
× Me. Alcohol (0·15g.)
+ Et. Alcohol (0·46g.)
○ Glycol (0·05g.)
□ Glycerol (0.07g.)
GRAMS. BENZOIN
TIME IN HOURS
- Fig. 16. -
POLYHYDRIC ALCOHOLS
(Effect on one-hour's yield)
Standard yield = 2.72g.
□ Erythrite
× Mannite
● Dulcite
○ Sorbite
◇ Inosite
GRAMS. BENZOIN

(see Fig. 16). The effect, however, does not increase with the amount of the alcohol added, probably because, these alcohols have a very limited solubility in benzaldehyde.

A comparison of the results obtained with the hydroxy-compounds shows that glycol and glycerol are more powerful accelerators than methyl and ethyl alcohols. Thus the accelerating effect appears to increase with the number of hydroxy-groups in the molecule of the compound added. A definite acceleration has been observed with 0·2% of polyhydric alcohols in benzaldehyde, 0·35% of glycerol and 0·5% of glycol.

It will be seen that the results with alcohols are much more complex than with inert solvents and do not admit of mathematical formulation. In all cases they accelerate the reaction, probably by increasing the quantity of potassium cyanide dissolved. But they tend, in certain quantities, to delay the start of the homogeneous reaction. It is this dual effect which makes the results complicated.

It should be remembered when discussing the results with hydroxy-compounds that they may react with benzaldehyde to form acetal derivatives.

Summary.

1. Inert organic solvents, when added to a mixture of solid potassium cyanide and benzaldehyde, precipitate a portion of the small quantity of potassium cyanide dissolved in the benzaldehyde, and thus cause the homogeneous autocatalytic reaction to proceed more slowly. They do not affect the heterogeneous reaction.

2. Hydroxy-compounds accelerate the benzoin reaction and the accelerating effect increases with the number of hydroxy groups.

PIGMENTS OF COTTON FLOWERS.

Part II. Uppam (*Gossypium herbaceum*)

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and
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Uppam (*G. herbaceum*) is an important dry-land cotton grown widely in South India since it is well adapted to withstand drought. The flower petal is yellow with deep crimson spot near the base. The petals used in this investigation were collected from the Central Farm, Coimbatore. At the close of the picking season the fresh flowers were collected, the petals removed and dried in the sun to crispness as rapidly as possible and then stored in cloth bags.

A. G. Perkin (1916) made a chemical study of the flower petals of *G. herbaceum* which he called the ordinary Indian yellow cotton flower and found that it contained Gossypitrin as the main component along with some isoquercitrin. It is not possible to find out exactly how his material differed from ours. He seems to have obtained his supply from North India. We are informed by the Cotton Specialist, Coimbatore that the North Indian Herbaceums are of longer duration, bushier in habit, often finer in quality and longer in staple ; the fibres are more difficult to gin than those in Madras. The flower petals, however, seem to be quite similar in appearance.

The results of our investigation are rather different from those of Perkin. We find that the chief components are gossypitrin (9 g. from 2200 g.) and quercetin (10 g.). Besides these we isolated in a fair yield (3 g.) a new glycoside which we find to be a monoglucoside of a new flavonol and small quantities of gossypetin (1 g.). We have not been able to detect the presence of any quercetin glucoside in the flowers. If any should be present, the quantity should be exceedingly small. When an alcoholic extract of the flowers was concentrated and allowed to stand for several days, a good amount of a crystalline solid was deposited. Perkin (1916) obtained a similar solid and found it to be easily soluble in water and inferred that it consisted of alkali metal salts of the pigment. We have observed that though this deposit is easily soluble in hot water, it dissolves rather sparingly in the

cold, that it gives very little residue on igniting in a platinum crucible and that its aqueous solutions are not alkaline to litmus. We find that it contained almost all the gossypitrin of the flowers in a fairly pure state. Our observations with these flowers do not therefore support Perkin's view that the pigments are present in them as alkali metal salts of the glucosides.

A detailed study of the new glycoside will be published later as soon as its nature is known definitely. Our samples of gossypitrin and gossypetin agree closely in properties and reactions with those isolated by Perkin and the aglucone synthesised by Baker, Nodzu and Robinson (1929). We have adopted Robinson's method of examining the colour reactions in buffer solutions of varying p_H and we find that our sample of gossypetin produces the same colour effects as recorded by him. This method gives useful results with gossypitrin also and easily distinguishes between the two. Our samples of gossypitrin and its acetyl derivative melt higher than those of Perkin probably due to their being purer.

Experimental.

Isolation of Gossypitrin.—Dry petals of *G. herbaceum* (2200 g.) were powdered, extracted repeatedly with boiling rectified spirits till the pigments were completely removed and the alcoholic extract concentrated to about 800 c.c. On allowing it to stand for some days a large quantity of deep yellow crystalline solid (needles) was deposited (*cf.* Perkin, 1916). It was not easily soluble in cold water or alcohol but dissolved readily on heating and crystallised out on cooling. The aqueous solution was neutral to litmus (rather faintly acidic). Ignition of the crude substance in a platinum crucible gave a very small quantity of ash which consisted mostly of alkali chlorides. It did not therefore appear to be a metallic salt of a glycoside pigment.

The crystalline sold was filtered, washed with a little alcohol and boiled with a sufficiently large quantity of water (about 800 c.c.). The yellow pigment dissolved and tarry impurities floated on the top. The hot solution was carefully decanted on to a filter and filtered. The resin was washed with a small quantity of hot water and the washings added to the original filtrate. On allowing the solution to cool overnight a large mass of golden yellow crystals was obtained. It was filtered and washed with a small quantity of water. A second crop was obtained by concentrating the mother liquor on a water-bath to 100 c.c. and allowing it to stand for two days. After one recrystallisation from water this sample resembled the previous one closely. The two put together weighed 15 g. It was, however, impure since the melting point was rather indefinite. After two crystallisations from aqueous pyridine it sintered and shrank at about 202° C. and melted

at 237–38° C. (yield 9 g.). It was sparingly soluble in glacial acetic acid and could easily be crystallised from it when mixed with some water. But the best method of further purifying it was to boil it up with a small quantity of dilute acetic acid. This removed some brown impurities and the solid now melted at 250–52° C. (decomp.). One further recrystallisation from boiling dilute acetic acid gave yellow needles melting at 251–52° C. without any previous sintering. (Found in air dried specimen: C, 48·3; H, 4·8; $C_{21}H_{20}O_{13}$, $2H_2O$ required C, 48·8; H, 4·7%). The substance was a hydrate. We could not get any form melting at 203° C. and acetone did not produce any definite change in the pure specimen. We, however, noticed that when the above pure sample was crystallised again from pyridine, the product sintered strongly and showed marked shrinking at about 203° C., though it melted down only at 250° C. The pure substance was sparingly soluble in alcohol, acetone, and glacial acetic acid but dissolved easily in hot dilute acetic acid and in pyridine. The colour reactions of our specimen agree entirely with the observations of Perkin. Aqueous lead acetate gives a deep red precipitate and ferric chloride gives an olive green colour. We find that alkali colour reactions are best observed by using buffer solutions of varying p_H and the reactions of gossypitrin contrast clearly with those of gossypetin (Baker, Nodzu and Robinson, 1929) as shown below:

Colour Reactions.

p_H	Gossypetin	Gossypitrin
6·8	Goes into solution very slowly producing a greenish yellow colour. In about 2 hours a green amorphous solid separates out. After 24 hours a colourless liquid with a dirty green precipitate at the bottom. No further change.	Substance is unaffected.
8·0	Dissolves rapidly to a yellow solution. In 3 minutes becomes pure green, then slowly opaque and dark and in about ½ hour turns brown purple. In 24 hours goes into a pale yellowish green liquid with a green precipitate at the bottom; After 48 hours colourless liquid with a green precipitate.	Yellow solution rapidly changes (½ minute) to yellowish green and in another ½ minute becomes bright emerald green which slowly fades. After 24 hours it is brown red and after 48 hours very faint brown.

p_H	Gossypetin	Gossypitrin
8·6	Yellow solution rapidly goes green which is fairly stable and slowly turns blue. After 1½ hours signs of purple appear and the solution is rather opaque. After 24 hours pale yellowish green liquid with green precipitate; after 48 hours colourless liquid and a green precipitate.	Yellow solution immediately going into green and then to emerald green which fades rapidly. In 10 minutes all green was lost, it was then brownish yellow fading slowly. After 24 hours pale brown red and no change thereafter.
9·8	Yellow solution. In a few seconds deep green, further 2 minutes pure blue which was stable for about 1½ hours. After 24 hours very faint blue and 48 hours colourless with a small precipitate.	Yellow solution going immediately to green and emerald green and rapidly fading. In 10 minutes loses all green and becomes brownish yellow rapidly fading. After 24 hours pale brown red and no further change.
11·0	Yellow-green-blue-deep blue very rapidly fading to pale blue. In ½ hour pale greenish blue, fading. After 24 hours very pale yellow brown and after 48 hours colourless with no precipitate.	Yellow, immediately goes into yellowish green, after 2 minutes goes yellowish brown and fades rapidly. In 5 minutes pale brownish yellow. In 24 hours faint brown red and no further change.

Gossypitrin is affected only at a higher p_H than the aglucone; its most brilliant colour is emerald green and it does not show any blue or purple whereas the brilliant effect of gossypetin is blue. The glucoside undergoes the changes and loses colour more rapidly than gossypetin. Further the green precipitate that is formed as an end product in the case of gossypetin is not formed with the glucoside.

Our sample of gossypitrin gives with *p*-benzoquinone, a maroon coloured gossypitrone which exhibits the same behaviour as described by Perkin. The acetyl derivative of the glucoside was obtained by boiling with acetic anhydride with or without sodium acetate and the product was purified by crystallisation from acetic anhydride and alcohol mixture. It was obtained as colourless needles, m.p. 240–44° C. (*cf.* Perkin 226–28° C.).

Hydrolysis to Gossypetin.—The glucoside was hydrolysed by boiling with 7% sulphuric acid for 2 hours and a good yield of the crystalline aglucone

was obtained. It was easily recrystallised from rectified spirit and it came out as yellow flat needles which grow dark and decompose at about 310° C. (Found in air dried specimen : C, 48·5 ; H, 4·6 ; $C_{15}H_{10}O_8$, $3H_2O$ required, C, 48·4 ; H, 4·3%). The hexa acetate crystallised from alcohol as colourless rhombohedral plates melting at 228–30° C. agreeing with the melting point recorded by Perkin for the natural specimen and by Baker, Nodzu and Robinson (*loc. cit.*) for the synthetic one. As the other product of hydrolysis of the glycoside, glucose was isolated as the osazone. Our sample of gossypetin gave colour reactions with sulphuric acid, lead acetate, ferric chloride and benzoquinone identical with those recorded by previous workers.

Isolation of a new glycoside.—The alcoholic mother liquor left after the removal of gossypitrin was again distilled on a water-bath in order to remove as much alcohol as possible and then treated with a large volume of water. The whole mixture was poured on to an evaporating basin and most of the remaining alcohol removed by heating on a water-bath. A brown red solution was produced along with a lot of tarry matter. By careful filtration of the hot solution most of the resin was removed and on allowing the filtrate to stand for two days a good amount of a yellow crystalline solid mixed with some resin separated out. It was filtered and twice recrystallised from hot water when it appeared as a greenish yellow solid. After three crystallisations from dilute pyridine, it was quite pure and appeared as yellow needles, m.p. 247–49° C. (yield 3 g.). It was found to be a new glycoside different from gossypitrin and quercimeritrin. A detailed report on this substance will be published later.

The mother liquors obtained in the course of the purification of the new glycoside were concentrated on a water-bath and extracted with ether repeatedly. The extraction was rather slow and the ether layer continued to become yellow even after 5 extractions. On evaporating the ether extract a yellow crystalline solid was obtained which crystallised out of rectified spirits as yellow needles, m.p. 310–12° C. and gave an acetyl derivative melting at 195° C. It was identified as quercetin (0·2 g.). From the aqueous solution left after ether extraction no definite substance could be obtained by concentration. It was therefore boiled with 7% sulphuric acid for 2 hours. The solution was filtered hot in order to separate resin and when it was cooled a yellow crystalline precipitate was formed mixed with some resin. It was, therefore, repeatedly extracted with ether and the ether solution evaporated. A yellow solid was obtained which easily crystallised out of alcohol as needles, m.p. 250–70° C. (yield 0·5 g.). It was obviously a mixture of aglucones. It was therefore acetylated and the product crystallised from alcohol. Of the two fractions which were isolated, the

more soluble fraction consisted of quercetin pentacetate which was rendered quite pure by one further recrystallisation; the less soluble fraction consisted of gossypetin hexa-acetate which was also obtained quite pure by one further crystallisation. Glucose was detected in the solution after removing the aglucones. Whether quercetin obtained here was originally present free or in the form of an easily soluble glucoside is a question which cannot be answered definitely. Since quercetin could be obtained from the solution even before hydrolysis and the quantity of quercetin obtained after hydrolysis in the form of the acetyl derivative was very small (about 0·1 g.), it could be surmised that no appreciable amount of quercetin glucoside could have been present.

Neutral lead acetate fraction: Isolation of Quercetin.—The original aqueous mother liquor left after the separation of the new glycoside was now treated with excess of neutral lead acetate with vigorous shaking. After allowing to stand for a day the orange red precipitate was filtered, washed with water and the pigment liberated by passing hydrogen sulphide into an aqueous suspension of the lead salt. Lead sulphide was filtered off, the precipitate again extracted with hot water and the collected water extracts concentrated on a water-bath. Crystals were collected in four fractions and each fraction separately examined. Each fraction was found to be mixed up with a good amount of resin. Repeated crystallisation from aqueous pyridine produced yellow crystalline substances. The first and second fractions were found to yield the same product—yellow needles, m.p. 310–12° C. which yielded an acetyl derivative, m.p. 197–98° C. Its identity with quercetin was established by the determination of the mixed melting points with quercetin and penta acetyl quercetin obtained from *G. herbaceum* and by a comparison of colour reactions. Yield of quercetin was 10 g. The mother liquor from the crystallisation of these fractions was extracted repeatedly with ether. The ether extract gave a crystalline yellow solid which no crystallisation from alcohol melted indefinitely between 240–70° C. It was obviously an impure aglucone. So it was acetylated and the acetyl derivative crystallised from rectified spirits. Acetyl gossypetin m.p. 228–30° C. (mixed m.p. the same) could be obtained pure (0·2 g.). After ether extraction the aqueous layer was boiled with 7% sulphuric acid for 2 hours and from the highly brown semi-solid that was produced some more gossypetin acetate (0·3 g.) was isolated by acetylation and repeated recrystallisation from alcohol. No other compounds could be separated.

The third and fourth fractions consisting of about 10% of the whole of the neutral lead acetate precipitate were found after two recrystallisations from water and subsequently from dilute pyridine to melt above 290° C.

(yellow needles) but did not give a sharp melting point. They were therefore acetylated, when they yielded readily pure acetyl gossypetin (0·5 g.).

Basic lead acetate fraction.—The filtrate left after isolating the neutral lead acetate precipitate was then treated with a large excess of basic lead acetate. Comparatively small quantity of a lemon yellow precipitate was obtained. When this was decomposed with hydrogen sulphide about 1 g. of a crude pigment was produced. This was identified as quercetin after repeated recrystallisation and comparison with an authentic specimen.

Summary.

The flower petals of the Uppam cotton plant (*G. herbaceum*) contain as their main components gossypitrin and quercetin. An appreciable quantity of a new glycosidic pigment and a small quantity of gossypetin were also isolated. Uppam petals, therefore, differ in their composition from those of *G. herbaceum* examined by Perkin who probably obtained his supply of the petals from the North Indian variety. His results indicated that gossypitrin was the main component and that isoquercitrin was present in small quantities.

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DETERMINATION OF ULTRASONIC VELOCITY IN 52 ORGANIC LIQUIDS.

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1. *Introduction.*

An important new field of research was opened up by Langevin when he applied the piezo-electric property of quartz and electrical oscillating circuits to the production of high-frequency sound-waves. Of the methods based on the use of the piezo-electric oscillator for the measurement of ultrasonic velocity in liquids we may mention three: (1) the acoustic interferometer invented by Pierce[1] and used amongst others by Freyer, Hubbard and Andrews[2]; (2) the method of the diffraction of light by sound waves originated by Debye and Sears[3] in America and by Lucas and Biquard[4] in France; and (3) the "Schlieren method" developed by Hiedemann, Bachem and Asbach[5] in a series of papers.

Amongst these the method of Debye-Sears and of Lucas-Biquard is very simple, precise and rapid. In the present investigation it has been applied to the accurate determination of supersonic velocity in a large number of organic liquids.

2. *Experimental Set-up.*

As the temperature coefficient of sound velocity in liquids is rather high, it is essential that the experiments should be made at a fairly constant temperature. All the experiments described in the present paper were conducted in an underground room, in which the temperature remained very steady, there being no fluctuation of temperature greater than 1° C. from day-to-day, and more than about half-a-degree in the course of a day.

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The oscillator set-up is almost the same as the one used by Lucas and Biquard in their investigations. Two power valves of high wattage, each of 60, are connected push-pull to give greater input at a steady rate. The diagram of connections given below is the well-known Hartley circuit, slightly modified to suit the conditions of experiment.

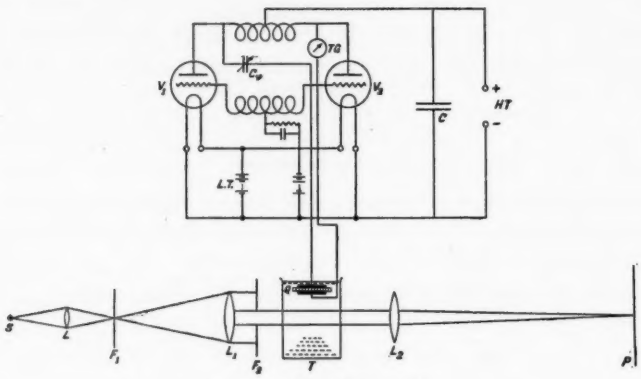


FIG. 1.

V_1 V_2 are the power valves, with their grids and anodes connected each to each by two coils. The oscillatory circuit consists of the anode coil, connected to a variable condenser, a piezo-quartz and a thermo-galvanometer in series. H.T. are the high-tension leads, the positive of which is connected to the middle of the anode coil. All other connections are the familiar ones used in wireless work.

The quartz piece is an X-cut crystal of 2 mm. thickness and of an area 20 by 20 mms. From Hund's expression, the fundamental comes out as 1·435 megacycles, as against 1·43 determined experimentally by taking the resonance curve for the quartz. In the experiments, a frequency very near the fifth harmonic of the crystal was used.

The optical arrangement followed was similar to one usually used in getting grating spectra. A monochromatic source of light was focussed on the slit of a collimator and the parallel beam of light, passing through a cell with plane-parallel windows, is focussed by an objective on a photographic plate. As a source, a mercury arc with filters was used. 4358 Å and 5461 Å of the mercury arc were used to check up each other.

Since the thickness of the camera lens was considerable, the distance lens-to-plate was measured from the centre of the lens to the photographic plate.

Size of the vessel.—In all experiments on the measurement of sound velocity by the Kundt's tube method, waves considerably larger than what have been used here, are excited and corrections become necessary due to the bore of the tube. But in experiments with very small wave-lengths, of the order of tenths of a millimetre, small vessels could be used without applying any correction whatever. A glass cell, holding about 50 c.c., was used throughout. The diameter of the cell being 3½ cm. while the wave-length of sound in the majority of liquids was roughly 0·02 cm., the ratio of the diameter of the liquid-chamber to wave-length is of such order that no tube corrections were found necessary.

However, an experiment using a bigger vessel was carried out and the results are given below.

TABLE I.

In CCl_4.

	Container vessel	Frequency in megacycles	Wave-length of sound in mms.	Velocity of sound in meters/second	Temp.
1	Small; capacity about 50 c.c.; depth 1 inch	7·32	0·1262	928·5	23°
2	Big trough; capacity about 250 c.c.; depth 2½ inches.	7·15	0·1298	929·0	23°

Determination of frequency.—The experimental arrangement, once set up, was not disturbed till all the liquids were employed, by simply removing the cell and changing liquids. The constants of the apparatus therefore remained the same.

A precision wave-meter of the General Radio Company, kindly lent to us by Mr. K. Srinivasan, Assistant Professor in the Electrical Technology Department of this Institute, was used to determine the frequency of oscillation. It was found to give very consistent readings at different times and on different days. All the experiments were conducted with $7{\cdot}32 \times 10^6$ cycles per second.

In order that the effect of damping of the oscillations by the superincumbent liquid might be negligible, the quartz crystal was suspended within less than half a centimetre below the surface of the liquid.

It was thought necessary to check up the wave-meter itself for accuracy. The circuit which included the quartz and a variable condenser could give

frequencies of oscillation ranging from 7·40 to 6·84 megacycles, and for different frequencies between these limits, we should get wave-lengths of sound inversely proportional to the former.

Incidentally this decided a point as to whether, when working near a resonance oscillation of a crystal, the oscillator controls the crystal. It is evident from the table given below that the crystal is maintained at the impressed frequency.

TABLE II.

In CCl_4 at 23° C.

Frequency in megacycles	Wave-length of sound in mms.	Velocity of sound in meters/second
7·40	0·1257	929·8
7·33	0·1267	928·5
7·22	0·1288	930·1
7·10	0·1310	930·3
6·99	0·1329	929·0
6·92	0·1344	930·1
6·84	0·1357	928·5
	mean value ..	929·5

Any variation in the input voltage and current is likely to alter the frequency even by ever so little, and it was made a point to see that both of them were adjusted to the same readings throughout the course of the work. However, fluctuations in the voltage were not much and even these small ones were quickly adjusted.

3. Results.

With the arrangements mentioned above and with due precautions, determinations were made of the ultrasonic velocity in 53 different liquids.

In the present investigation, the liquids were all distilled, some of them like methylene iodide under reduced pressure. Only the purest variety of chemicals from Kahlbaum, Merck or E. de Haen were employed, while in some cases Dr. Schukardt's preparations were used.

The temperature at which the velocity was determined has been noted against each liquid in the table.

Densities of all the liquids were also determined separately, using a specific gravity bottle, at the same temperature and are in good agreement with the standard values.

The velocities were calculated from the simple formula

$$\sin \theta = p\frac{\lambda}{\Lambda}$$

where θ is the angle of diffraction, measured as the ratio of the distance between two diffraction fringes, to the distance between the centre of camera lens and the plate,

λ is the wave-length of light used,

Λ is the wave-length of sound to be determined,

and p is the number of orders.

In all cases, the distance between a number of fringes, usually 6 or 8, was measured and then that between two calculated.

Both the 4358 Å and 5461 Å of the mercury lines were used as incident beams to check up against each other and the results obtained agree very well with each other.

The velocities measured are given in the table following for the frequency $7{\cdot}32 \times 10^6$ cycles which was employed throughout.

TABLE III.

Ultrasonic Velocity at $7{\cdot}32 \times 10^6$ *cycles per second.*

Liquids	Formula	Temp. in °C.	Density	Wave-length of sound in mms.	Velocity of sound in meters/second
Hexane (*n*) ..	C_6H_{14}	23°·0	0·6581	0·1521	1113
Heptane (*n*) ..	C_7H_{16}	23°·0	0·6812	0·1592	1165
Methyl alcohol ..	$CH_3{\cdot}OH$	23°·8	0·7921	0·1544	1130
Ethyl alcohol ..	C_2H_5OH	23°·5	0·7863	0·1649	1207
Propyl alcohol (*n*) ..	$C_3H_7{\cdot}OH$	24°·0	0·8011	0·1686	1234
Isopropyl alcohol ..	$CH_3{\cdot}CH{\cdot}OH{\cdot}CH_3$	23°·0	0·7850	0·1682	1231
Butyl alcohol ..	$CH_3{\cdot}(CH_2)_3{\cdot}OH$	23°·0	0·8082	0·1797	1315
Isobutyl alcohol ..	$(CH_3)_2{\cdot}CH{\cdot}CH_2OH$	23°·5	0·8011	0·1736	1271
Amyl alcohol(*n*) ..	$CH_3{\cdot}(CH_2)_4{\cdot}OH$	24°·0	0·8136	0·1840	1347
Methyl acetate ..	$CH_3{\cdot}COOCH_3$	24°·0	0·9282	0·1654	1211

TABLE III—(*Contd.*)

Liquids	Formula	Temp. in °C.	Density	Wave-length of sound in mms.	Velocity of sound in meters/second
Methyl propionate ..	$C_2H_5 \cdot COOCH_3$	24°·5	0·9112	0·1660	1215
Ethyl formate ..	$H \cdot COOC_2H_5$	23°·5	0·9048	0·1725	1263
Ethyl acetate ..	$CH_3 \cdot COOC_2H_5$	23°·5	0·8989	0·1623	1187
Ethyl propionate ..	$C_2H_5 \cdot COOC_2H_5$	23°·5	0·8837	0·1619	1185
Ethyl butyrate	$C_3H_7 \cdot COOC_2H_5$	23°·5	0·8768	0·1600	1171
Butyl formate ..	$H \cdot COOC_4H_9$	24°·0	0·9066	0·1638	1199
Acetone ..	$CH_3 \cdot CO \cdot CH_3$	22°·5	0·7910	0·1643	1203
Diethyl ketone ..	$C_2H_5 \cdot CO \cdot C_2H_5$	24°·0	0·8132	0·1795	1314
Methyl hexyl ketone..	$CH_3 \cdot CO \cdot C_6H_{13}$	24°·0	0·8170	0·1809	1324
Amylether (iso) ..	$[(CH_3)_2 \cdot CH \cdot CH_2 \cdot CH_2]_2O$	23°·5	0·7720	0·1613	1180
Acetic anhydride ..	$\begin{matrix} CH_3 \cdot CO \\ CH_3 \cdot CO \end{matrix} > O$	24°·0	1·075	0·1891	1384
Carbon disulphide ..	CS_2	23°·0	1·258	0·1570	1149
Carbon tetrachloride	CCl_4	23°·0	1·596	0·1269	928·5
Chloroform ..	$CHCl_3$	23°·5	1·487	0·1367	1001
Bromoform ..	$CHBr_3$	24°·0	2·889	0·1271	929·8
Methylene chloride ..	CH_2Cl_2	23°·5	1·336	0·1453	1064
Methylene bromide ..	CH_2Br_2	24°·0	2·453	0·1326	971·2
Methylene iodide ..	CH_2I_2	24°·0	3·323	0·1336	977·7
Ethylene chloride ..	$\begin{matrix} CH_2-Cl \\ \vert \\ CH_2-Cl \end{matrix}$	23°·0	1·255	0·1693	1240
Ethylene bromide ..	$\begin{matrix} CH_2-Br \\ \vert \\ CH_2-Br \end{matrix}$	24°·0	2·178	0·1385	1014
Ethylene glycol ..	$\begin{matrix} CH_2-OH \\ \vert \\ CH_2-OH \end{matrix}$	24°·0	1·103	0·2351	1721

TABLE III—(*Contd.*)

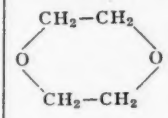
Liquids	Formula	Temp. in °C.	Density	Wave-length of sound in mms.	Velocity of sound in meters/second
Trimethylene bromide	CH_2-Br CH_2 CH_2-Br	23°·5	1·977	0·1563	1144
$\beta\,\beta$ dimethyl glutaric acid dimethyl ester	$CH_2-COOCH_3$ $C\cdot(CH_3)_2$ $CH_2-COOCH_3$	24°·0	1·038	0·1872	1371
Acetal ..	$CH_3\cdot CH(OC_2H_5)_2$	24°·0	0·8273	0·1550	1134
Dioxan .		24°·0	1·030	0·1883	1378
Benzene ..	C_6H_6	23°·0	0·8725	0·1790	1310
Toluene ..	C_7H_8	23°·0	0·8631	0·1803	1320
m-Xylene ..	C_8H_{10}	23°·0	0·8612	0·1822	1334
Chlorobenzene ..	C_6H_5Cl	23°·0	1·101	0·1778	1302
Nitrobenzene ..	$C_6H_5\cdot NO_2$	24°·0	1·199	0·2035	1490
Aniline ..	$C_6H_5\cdot NH_2$	24°·0	1·018	0·2298	1682
Anisol ..	$C_6H_5\cdot O\cdot CH_3$	24°·0	0·9865	0·2035	1489
Ethyl phthalate ..	$C_6H_4(COOC_2H_5)_2$	23°·0	1·121	0·2009	1471
Acetophenone ..	$C_6H_5\cdot CO\cdot CH_3$	24°·0	1·024	0·2102	1538
Pyridine ..	C_6H_5N	24°·0	0·9752	0·1978	1448
α-Picoline ..	$C_6H_4N\cdot CH_3$	24°·0	0·9508	0·1358	994·5
Cyclohexane .	C_6H_{12}	23°·0	0·7721	0·1718	1257
Cyclohexanone ..	$C_5H_{10}\cdot CO$	23°·5	0·9491	0·1968	1441
Cyclohexanol ..	$C_5H_{10}\cdot CH(OH)$	23°·5	0·9461	0·2216	1622
Cyclopentanone ..	$C_4H_8\cdot CO$	24°·0	0·9481	0·2014	1474

TABLE III—(*Contd.*)

Liquids	Formula	Temp. in °C.	Density	Wave-length of sound in mms.	Velocity of sound in meters/ second
Dipentene ..	$C_{10}H_{16}$	23°·8	0·8644	0·1815	1328
Tetralin ..	$C_{10}H_{12}$	24°·0	0·9681	0·2002	1465
Water (Double distilled) ..	H_2O	24°·0	0·9972	0·2041	1494

Of the liquids studied, data for velocity of sound are available for only 16 of them at different frequencies.

Investigations in the audio range have been carried out by Dörsing,[6] Busse[7] and others, using the well-known Kundt's tube method. Their values are taken from the *International Critical Tables*.

Freyer, Hubbard and Andrews[8] worked with the sonic interferometer, using a piezo-quartz with a fundamental at 414 kc. There are two points which require elucidation in their paper: (1) they employed a range of 0° C. to 50° C. and still used 414 kc. throughout this range, though the temperature correction is considerable when the crystal is vibrating along the electric axis, as pointed out by Dye, Lack and others; and (2) recently E. Grossmann[9] has pointed out that the half-wave-lengths which are measured by the interferometer no longer remain constant throughout from the quartz to the reflector, but depend on the distance mainly from the quartz. However, their results are given for comparison, corrected to 23° C.

Still more recently J. C. Swanson[10] working on pressure coefficients of sound velocity in liquids, has given the velocity at about 200 kc. and 20° C. for some organic liquids. His values are included in the table for comparison.

For water, the velocity was taken from a paper by Hubbard and Loomis[11] appearing in the *Philosophical Magazine* for 1928.

Bachem and Hiedemann[12] and Wyss[13] have also determined sound velocities for a few organic liquids.

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6 Dörsing, *Ann. der Phys.*, 1908, **25**, 227.
7 W. Busse, *Ann. der Phys.*, 1924, **75**, 657.
8 Freyer, Hubbard and Andrews, *J. A. C. S.*, 1929, **51**, 759.
9 E. Grossmann, *Phys. Zeit.*, 1934, **35**, 83.
10 J. C. Swanson, *J. Chem. Phys.*, 1934, **2**, 689.
11 Hubbard and Loomis, *Phil. Mag.*, 1928, **5**, 1177.
12 Bachem and Hiedemann, *Zeit. für Physik.*, 1935, **94**, 68.
13 R. Wyss, *Helv. Phys. Acta.*, 1934, **7**, 406.

TABLE IV.

Comparison of Velocities with those obtained by others (meters/second).

	Liquids	Freyer, Hubbard & Loomis. Freq. = 414 kc. Temp. = 23°C.	Author Freq. 7·32 ×10⁶ Temp. 23°C.	Audio Range, by Kundt's tube method From the *International Critical Tables*		J. C. Swanson Freq. 200 kc. Temp. 20°C.	Bachem and Hiedemann Freq. 5·20 ×10⁶ Temp. 25°C.
				Velocity	Temp. in °C.		
1	Benzene ..	1307	1310	1166	17°	1290	1299·6
2	Toluene ..	1314	1320	1327	20°·5	1313	1303·4
3	*m*-Xylene ..	....	1334	....	....	....	1322·0
4	CCl_4 ..	925	928·5	....	....	912	921·2
5	CS_2 ..	1147	1149	1161	15°	1136	
6	Chloroform ..	991	1001	983	15°	986	
7	Hexane ..	....	1113	1112	21°		
8	Heptane ..	1141	1165	....	....		
9	Chlorobenzene ..	1272	1302	1315	17°		
10	Ethyl alcohol ..	1155	1207	1275	15°		
11	Methyl alcohol ..	1111	1130	1143	19°		
12	Acetone ..	1175	1203	1189	20°·5		
13	Aniline ..	1646	1682	1676	21°	1640	
14	Bromoform ..	922	929·8	....	....		
15	Amyl alcohol ..	....	1347	1270	20°		
16	Nitrobenzene ..	....	1490	1506	18°		
17	Water ..	1495 at 24°C.	1494 at 24°C.	1433	15°		

4. *Discussion.*

A. Dependence of sound velocity on chemical constitution.

(i) A survey of the sound velocity measurements given in the table makes it clear that the aromatic compounds in general have higher velocities than the corresponding aliphatics in spite of the fact that their densities are higher. Cyclohexane and its derivatives come midway between the two classes.

(ii) The sound velocity in liquids of high density, *e.g.*, the halogen-substituted derivatives is low, but not as low as the increased density would

suggest. The effect of increased density is actually set off to a considerable extent by a diminution in the compressibilities.

(iii) Liquids with molecules having electric moment tend to exhibit higher sound velocities. This is exemplified by the alcohol series, the ketone series, acetic anhydride, nitrobenzene, aniline, acetophenone, cyclohexanol and water. Tetralin possesses a small electric moment and the sound velocity in it is higher than in either benzene or cyclohexane.

(iv) Lengthening of the molecule gives enhanced velocity. Heptane (*n*) though possessing higher density, shows definitely greater velocity than that of (*n*)-hexane. The normal alcohols form another series which show the dependence of velocity on the length of the hydrocarbon chain. It is, however, interesting to note that the iso-alcohol shows a lower sound velocity than that in the normal one, *e.g.*, isopropyl and isobutyl alcohols.

B. Dependence of sound velocity on frequency.

Freyer, Hubbard and Andrews were the earliest to use as high a frequency as 414 kc. to measure accurately sound velocities in liquids. No dispersion was noticed upto this range.

When the possibility of using still higher frequencies, with their optical examination, was opened up by Debye and Sears, and Lucas and Biquard, attention was confined mainly to three or four liquids to see whether there was any dispersion. They used frequencies upto 10^7 cycles per second and found no dispersion in CCl_4, toluene, benzene and water.

In the present investigation a large number of liquids have been included for which acoustic velocity data are available for the audio range. The frequencies used in some cases range from the audio to 200 kc., 414 kc. and $7{\cdot}32 \times 10^6$ cycles per second. An examination of the available data clearly points out to the fact, that allowing for temperature correction, there is no dispersion of sound velocity in the ranges investigated, excepting benzene, for which the discrepancy between the audio and the ultrasonic range seems to be too great to be real.

5. *Adiabatic Compressibilities.*

It is well known that V, the velocity of sound, ρ the density and $\beta\phi$ the adiabatic compressibility are connected together by the relation

$$V = \sqrt{\frac{1}{\beta\phi\rho}} = \sqrt{\frac{\gamma}{\beta_T\rho}}$$

where β_T is the isothermal compressibility and γ the ratio of specific heats. Hence the latter quantity also can be determined if the two compressibilities are known.

$\beta\phi$ and γ, wherever the isothermal compressibilities are known, have been calculated for all the liquids, using the experimentally determined values of the densities.

Careful determinations of $\beta\phi$ by the piezometer method were made by Tyrer[14] in 1913 and 1914, and laterly Shiba[15] using one piezometer to determine both $\beta\phi$ and β_T has made investigations on 29 organic liquids. Shiba himself admits in his paper that his results give higher values than those given by Tyrer. Furthermore, he was concerned more with ratios and differences of the two compressibilities, and therefore his values are not given here for comparison. Tyrer's values, as computed for the particular temperature, are given.

Values of β_T have been determined experimentally by Pagliani and Palazzo (P and P), Röntgen (Rönt), de Heen (de H), Bartoli (Bart), Drecker (Dr), Smith (Sm), Parsons and Cook (P and C), J. Hebeisen (Heb) and K. Schmidt (Sch). Their values are taken from the *International Critical Tables* and Cohen and Schut's "Piezochemie", and corrected to the temperature at which the sound velocity for the liquid was determined. They are mostly for 1 to 2 atmospheres, while in some it is upto 5–7 atmospheres.

In the table the initials denote the author from whom the values were taken, as indicated above in brackets.

The agreement in $\beta\phi$ between Tyrer's and the author's is good in all cases except for ethylene chloride, where the discrepancy is marked.

TABLE V.

Adiabatic Compressibilities for Liquids (at Temperatures given in Table III).

Liquids	Adiabatic compressibility $\beta\phi\times10^6$		Isothermal Compressibility		Ratio of Specific heats $\frac{\beta_T}{\beta\phi}=\gamma=\frac{C_p}{C_v}$
	Author's calculated values	Tyrer's experimentally determined values	$\beta_T\times10^6$	Taken from	
Hexane (*n*) ..	122·7		152·5	Sch.	1·214
Heptane (*n*) ..	108·1		134	Bart.	1·240
Methyl alcohol ..	98·9		116·1	P and C	1·174

[14] Tyrer, *J. C. S.*, 1914, **105**, 2539.

[15] H. Shiba, *Journal of the Inst. of Phys. and Chem. Research in Japan*, 1931, **16**, 205.

TABLE V—(*Contd.*)

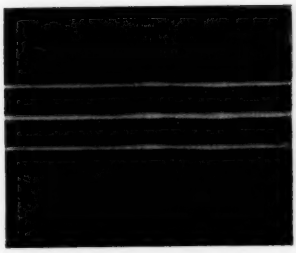
Liquids	Adiabatic compressibility $\beta_\phi \times 10^6$		Isothermal compressibility		Ratio of specific heats $\frac{\beta_\tau}{\beta_\phi} = \gamma = \frac{C_\phi}{C_v}$
	Author's calculated values	Tyrer's experimentally determined values	$\beta_\tau \times 10^6$	Taken from	
Ethyl alcohol ..	87·3		*106* 107	Sm. P and P	1·214
Propyl alcohol (*n*) ..	81·9		95·2	P and P	1·162
Isopropyl alcohol ..	84·1		106·9	Rönt.	1·272
Butyl alcohol ..	71·5		93·4	Rönt.	1·160
Isobutyl alcohol ..	77·4		98·1	P and P	1·268
Amyl alcohol ..	67·8		89·7	P and P	1·323
Methyl acetate ..	73·5				
Methyl propionate ..	74·3				
Ethyl formate ..	69·3				
Ethyl acetate ..	79·0				
Ethyl propionate ..	80·6				
Ethyl butyrate ..	83·2		103·8	de H	1·247
Butyl formate ..	76·8				
Acetone	87·4		123·4	Heb.	1·413
Diethyl ketone ..	71·2				
Methyl hexyl ketone	69·8				
Amyl ether (iso) ..	93·0				
Acetic anhydride ..	48·6				

TABLE V—(*Contd.*)

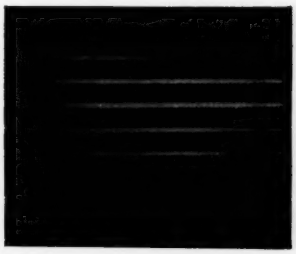
Liquids	Adiabatic compressibility $\beta_\phi \times 10^6$		Isothermal compressibility		Ratio of specific heats $\frac{\beta_\tau}{\beta_\phi} = \gamma = \frac{C_\phi}{C_v}$
	Author's calculated values	Tyrer's experimentally determined values	$\beta_\tau \times 10^6$	Taken from	
Carbon disulphide ..	60·2	60·9	95·0	Dr.	
			93·4	P and P	1·552
Carbon tetrachloride	72·6	73·7			
Chloroform ..	67·1	68·6	*100·6*	Sch.	1·499
			103·2		
Bromoform ..	40·0				
Methylene chloride ..	66·2				
Methylene bromide ..	43·2				
Methylene iodide ..	31·5				
Ethylene chloride ..	51·8	56·1			
Ethylene bromide ..	44·7		60·3	de H	1·349
Ethylene glycol ..	30·7				
Trimethylene bromide	38·6				
$\beta\beta$ demethyl glutaric acid dimethyl ester	51·3				
Acetal	94·0				
Dioxan	51·1				
Benzene ..	66·8	66·8	92·1	P and P	1·379

TABLE V—(*Contd.*)

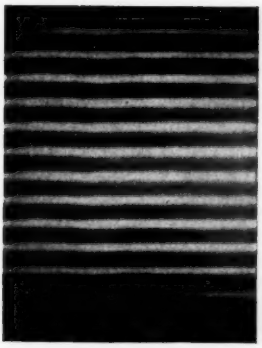
Liquids	Adiabatic compressibility $\beta\phi \times 10^6$		Isothermal compressibility		Ratio of specific heats
	Author's calculated values	Tyrer's experimentally determined values	$\beta_\tau \times 10^6$	Taken from	$\frac{\beta_\tau}{\beta_\phi} = \gamma = \frac{C_p}{C_v}$
Toluene	66·5	68·4	*89·4*	Sch.	
			87·1	de H	1·345
			89·5	P and P	
m-Xylene	65·3	66·2			
Chlorobenzene ..	53·6	56·2	*73·4*	Sch.	
Nitrobenzene ..	37·6	40·9	48·1	Sch.	1·279
Aniline	34·7	36·6	45·2	Heb.	1·302
Anisol	45·7		64·5	Heb.	1·411
Ethyl phthalate ..	41·2				
Acetophenone ..	41·3				
Pyridine	48·9				
α-Picoline ..	106·4				
Cyclohexane ..	81·9	82			
Cyclohexanone ..	50·8				
Cyclohexanol ..	40·2				
Cyclopentanone ..	48·6				
Dipentene ..	65·5				
Tetralin ..	48·1				
Water (double distilled) ..	44·9	45·5			



Benzene 5461Å



Toluene 4358Å



m-Xylene 4358Å

Cyclohexane 5461Å

Carbon tetrachloride 5461Å

From the experimentally determined values of β_T and the author's value for $\beta\phi$, γ the ratio of specific heat in liquids has been calculated. It is however too premature to draw any conclusion therefrom, as the data are quite insufficient.

6. *Summary.*

The paper gives determinations of ultrasonic velocities at $7{\cdot}32\times10^6$ cycles for 52 organic liquids and water by the method of diffraction of light by ultrasonic waves. It is shown how the velocity depends on chemical constitution.

Included in the paper are adiabatic compressibilities for all the liquids studied, calculated from the well-known formula.

The author's best thanks are due to Professor Sir C. V. Raman, Kt., F.R.S., N.L., for his constant help and encouragement in the work. He thanks also Dr. P. C. Guha, Acting Professor of Organic Chemistry, for a loan of many of the organic liquids studied in this paper.

KINETICS OF THE REACTION BETWEEN α BROMPROPIONATE AND SILVER IONS.

A Heterogeneous Reaction taking place on the Surface of Silver Bromide.

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Received October 15, 1935.

Beckerts and Oddo[1] showed that halogen-substituted propionic acids react with silver nitrate quantitatively in the manner indicated by the equation

$$CH_3.CH.X.COOH + AgNO_3 + H_2O = CH_3.CH.(OH).COOH + AgX + HNO_3.$$

In the course of his investigations on the reactivity of halogens in substituted fatty acids, Senter[2] made a brief study of the reaction between α brompropionate and silver ions and obtained very interesting kinetic data. He found, in fairly dilute solutions, that the bimolecular velocity constants gradually increased as the reaction progressed and the initial velocity constant was found to be dependent upon the dilution of the solutions. Senter attributed the increase in velocity constant with the progress of the reaction to the catalytic effect of the silver halide formed during the course of the reaction and the greater initial velocity in the more dilute solutions to the greater electrolytic dissociation of the reacting salts.

The reaction presents interesting features viewed from different standpoints. First, here we have a reaction which is essentially a hydrolytic one. Senter[3] has shown that sodium brompropionate does not very readily undergo the hydrolytic change in pure aqueous solutions even at fairly high temperatures. In mixtures of sodium brompropionate and silver nitrate, however, the reaction proceeds with great rapidity even at ordinary temperatures. The accelerating effect of silver nitrate in such halogen replacements appears to be quite well known[4] but its mechanism has not been elucidated. Secondly, if, as has been observed by Senter,[2] the silver bromide formed in the course of the reaction exerts a catalytic effect also, the rapid hydrolytic reaction is probably the result of a composite catalytic action—homogeneous and heterogeneous. The present investigation was undertaken with a view to elucidate the probable mechanism of the reaction, by a detailed kinetic study.

Experimental.

Senter pointed out that during the course of the reaction, the silver bromide formed, which remains in suspension for some time, coagulates after a while and settles down at the bottom or floats at the top of the solutions. The conditions of experiment will not, therefore, be uniform and this difficulty prevents a systematic treatment of the data. Preliminary experiments showed that in solutions much more dilute than the ones employed by Senter the silver bromide suspension could remain quite stable for some hours, without coagulation, if the silver bromide is formed in presence of excess of silver nitrate. Since in the present investigation, silver nitrate happens to be one of the reacting components and always remains in excess during the progress of the reaction, it is possible to test the catalytic effect of silver bromide under fairly reproducible conditions.

Senter's study was confined to two dilutions; the concentrations of silver nitrate and sodium brompropionate were N/30 each in one case and N/60 each in the other. He followed the reaction by titrating portions of the reaction mixture against N/50 ammonium thiocyanate solution, thus determining the amount of silver nitrate remaining in the mixture at any given time. In the present work this method has been adopted only in a few cases, where the concentration of silver nitrate in the reaction mixture was in the neighbourhood of N/50. In all other cases the reaction has been followed by estimating the amount of acid liberated in the reaction at different intervals in the following way. At intervals a definite quantity of the reaction mixture was pipetted out and excess of potassium iodide was added to it to arrest the reaction immediately; potassium iodate was next added to the mixture. Potassium iodide and iodate together quantitatively react with the hydrogen ion formed in the reaction and liberate an equivalent amount of iodine. The iodine thus liberated was titrated against standard N/100 or N/200 thiosulphate solution. This procedure has the double advantage of enabling us to arrest the reaction at any desired moment and to study the reaction in very dilute solutions.

The experiments were all carried out in bottles covered with black paint on the outside, to prevent the silver bromide from being acted upon, as far as possible, by the diffuse light of the laboratory. It may be mentioned, however, that a few experiments carried out in uncovered bottles gave the same results as in covered bottles. The bottles containing the reaction mixtures were kept in an electrically regulated thermostat. All the experiments described in this paper were carried out at 27° C.

The salts used in this study were all purified by recrystallisation and all the solutions were prepared in conductivity water obtained from a Bartley's still.

Tables I and II contain results obtained with the same concentrations of the reactants, 0·03 N sodium brompropionate and 0·02 N silver nitrate. In the first case (Table I) the reaction was followed by titrating 25 c.c. of the reaction mixture against N/50 potassium thiocyanate and in the second case (Table II) by treating the same volume of the reaction mixture with potassium iodide and iodate mixture and titrating the liberated iodine against N/50 sodium thiosulphate. In both these experiments the first titration was performed two minutes after the reactants were mixed together. The two experiments were carried out at different times to compare the results obtained by adopting the different methods of analysis.

TABLE I.

Time in minutes	c.c. $AgNO_3$
0	23·00
5	19·80
10	16·40
15	13·20
20	10·50
25	9·85
30	9·50
35	9·40

TABLE II.

Time in minutes	c.c. Hypo.	c.c. $AgNO_3$
0	2·10	22·90
5	5·35	19·65
10	8·55	16·45
15	12·05	12·95
20	14·70	10·30
25	15·25	9·75
30	15·35	9·65
35	15·45	9·55

It will be observed that the figures at different corresponding intervals in the two tables do not differ appreciably from one another. After about twenty minutes it was observed in both the experiments that coagulation of silver bromide commenced, a portion of it sinking to the bottom and a portion rising to the surface. This was accompanied, as will be seen from the tables, by a fall in the velocity of the reaction.

The bimolecular velocity constants calculated from the data in Table I are shown in Table III.

TABLE III.

Time in minutes	c.c. $AgNO_3$	c.c. brom-propionate	K_2
0	23·00	35·50	
5	19·80	32·30	1·104
10	16·40	28·90	1·325
15	13·20	25·70	1·546
20	10·50	22·50	1·638

It is clear from these results that the velocity of reaction increases as the reaction progresses, indicating the existence of an autocatalytic effect. This result is very similar to the one obtained by Senter.[2]

Further experiments were carried out in more dilute solutions to find out the conditions under which the silver bromide formed in the reaction remains as a stable suspension almost upto the end of the reaction, in the reaction mixtures. The results are recorded in the tables below. Figures in column four of the tables are the bimolecular velocity constants calculated from the data in the first three columns.

TABLE IV.

Concentration of sodium brompropionate 0·015 N $=b$
Concentration of silver nitrate 0·01 N $=a$
25 c.c. titrated each time against N/50 thiosulphate.

Time in minutes	$(a-x)$	$(b-x)$	K_2	$(c+x)$	K_3
0	11·65	17·90		0·85	
5	10·90	17·15	0·8496	1·60	$9·93 \times 10^2$
10	8·70	14·95	2·2402	3·80	10·34 ,, ,,
15	7·45	13·70	2·3920	5·05	11·15 ,, ,,
20	6·20	12·45	2·6726	6·30	10·54 ,, ,,
*25	5·05	11·30	3·0038	7·45	10·02 ,, ,,
30	4·65	10·90	2·7516		10·39 ,, ,, mean value
40	4·55	10·80	2·1758		

* Coagulation became perceptible at this stage.

TABLE V.

Concentration of sodium brompropionate 0·006 N = b
Concentration of silver nitrate 0·004 N = a
25 c.c. titrated each time against N/100 thiosulphate.

Time in minutes	$(a-x)$	$(b-x)$	K_2	$(c+x)$	K_3
0	9·30	14·30		0·70	
5	8·85	13·85	1·7940	1·15	$4·59 \times 10^3$
10	8·15	13·15	2·4035	1·85	3·49 ,, ,,
15	7·35	12·35	2·9510	2·65	4·84 ,, ,,
20	6·60	11·60	3·3465	3·40	4·56 ,, ,,
25	5·85	10·85	3·7490	4·15	4·36 ,, ,,
30	5·20	10·20	4·0560	4·80	4·14 ,, ,,
40	3·75	8·75	5·2095	6·25	4·10 ,, ,,
50	2·75	7·75	6·0536	7·25	3·99 ,, ,,
60	1·85	6·85	7·3151	8·15	4·26 ,, ,, mean value

At the dilutions in the last three cases (Tables V–VII) the silver bromide formed during the course of the reaction remained as a fine suspension and no coagulation was observable during the time the experiments were in progress.

Experiments carried out at greater dilutions showed that the initial formation of silver bromide was very slow and that during the first five or six hours even ten per cent. of the silver nitrate in the reaction mixture had not reacted with the brompropionate.

The results in the above tables show that the initial velocity of the raction is much faster in solutions in which the reactants are present in greater concentrations. These results, therefore, do not support Senter's inference[2] (based on only two experiments) that the initial velocity is greater at greater dilutions in this reaction.

TABLE VI.

Concentration of sodium brompropionate 0·003 N = b
Concentration of silver nitrate 0·002 N = a
25 c.c. titrated each time against N/200 thiosulphate.

Time in minutes	$(a-x)$	$(b-x)$	K_2	$(c+x)$	K_3
0	9·65	14·65		0·35	
10	9·25	14·25	0·1900	0·75	$1·384 \times 10^4$
20	8·65	13·65	0·2415	1·35	1·278 ,, ,,
30	7·70	12·70	0·2789	2·30	1·255 ,, ,,
40	6·55	11·55	0·3772	3·45	1·234 ,, ,,
50	5·45	10·45	0·4683	4·55	1·196 ,, ,,
60	4·35	9·35	0·5784	5·65	1·182 ,, ,,
70	3·20	8·20	0·7461	6·80	1·114 ,, ,,
					1·250 ,, ,, mean value

TABLE VII.

Concentration of sodium brompropionate 0·0015 N = b
Concentration of silver nitrate 0·0010 N = a
50 c.c. titrated each time against N/200 thiosulphate.

Time in minutes	$(a-x)$	$(b-x)$	K_2	$(c+x)$	K_3
0	9·65	14·65		0·35	
30	9·30	14·30	0·1917	0·70	$1·675 \times 10^4$
60	9·00	14·00	0·2319	1·00	1·30 ,, ,,
120	7·80	12·80	0·3191	2·20	1·22 ,, ,,
180	5·70	10·70	0·5865	4·30	1·28 ,, ,,
270	4·30	9·30	0·6610	5·70	1·06 ,, ,,
330	3·30	8·30	0·7658	6·70	1·02 ,, ,,
					1·26 ,, ,, mean value

These results at the same time indicate, beyond doubt, that in solutions in which the silver bromide formed in the reaction does not coagulate and settle down, the velocity of reaction, as judged by the bimolecular velocity coefficient K_2, uniformly increases with the progress of the reaction. It is quite obvious from this that the reaction product or products exert a catalytic effect on the reaction. That the catalyst is the finely suspended silver bromide formed in the reaction is evidenced by the arrest of the reaction, observable from data in Tables I and II and IV when the silver bromide coagulates and settles down, the tremendous slowing down of the reaction rate being due to the large diminution in the surface area of the particles on coagulation.

In very dilute solutions (below 0·001 N) the reaction does not start at all for quite a long time and until some silver bromide is formed the speed of the reaction is immeasurably small; which shows that the reaction in the homogeneous phase is of a negligible order of magnitude. In other words, the reaction appears to proceed almost entirely on the surface of the silver bromide particles. The bimolecular velocity coefficient K_2 in the above tables, therefore, apart from indicating the general dependency of the rate of reaction on the amount of silver bromide in suspension in the reaction mixture, has very little quantitative significance unless it is considered in relation to the surface area of the seat of reaction.

It has been pointed out above that the reaction does not start at all in extremely dilute solutions for quite a long time and that the presence of at least a trace of silver bromide appears to be essential to initiate the reaction. It is important to bear in mind that the hydrolytic process is one that can and does proceed in solutions containing only sodium brompropionate; but the process is an extremely slow one and the greater the dilution of sodium brompropionate the slower the hydrolysis. In more concentrated solutions of this salt, the amount of hydrobromic acid formed in the first few seconds or even minutes is probably quite sufficient to produce enough of silver bromide in the heterogeneous phase (on the addition of silver nitrate), to start the rapid catalysed reaction; whereas in very dilute solutions it will take considerable time for enough bromide ion to form from homogeneous hydrolysis before the solubility product of silver bromide is reached and a certain amount of the halide separates in the heterogeneous phase.

A few experiments were carried out, both in moderately concentrated solutions and in dilute solutions, to see if silver bromide prepared as a colloidal solution when added to a solution of sodium brompropionate (without the addition of any silver nitrate) would accelerate the hydrolytic process. It was found that the amount of hydrolysis brought about was not more

than 2–3 per cent. of the total concentration of the brompropionate in the course of about 24 hours. It was also observed that the suspensions were very unstable and coagulation set in in the first few hours after the mixtures were made. It would therefore appear that silver ions absorbed on the surface of silver bromide particles are the effective agents in accelerating the reaction; the actual reaction probably takes place between brompropionate and silver ions both held adsorbed on the surface of the silver bromide particles (the water necessary for the reaction being available in abundance all round the particles). We thus arrive at a qualitative picture of the possible mechanism of the reaction.

Since it is observed that in solutions in which silver bromide remains as a stable suspension, the bimolecular velocity constant increases steadily with the progress of the reaction, *i.e.*, with the progressive addition of silver bromide to the reaction system, if we make an assumption that the velocity of reaction is proportional to the amount of silver bromide present in suspension at any interval—which is tantamount to making an assumption, in view of the mechanism of the reaction pictured in the previous paragraph, that the effective surface of silver bromide in suspension is proportional to its concentration expressed in molecules per litre—the rate of reaction could be expressed by the equation

$$dx/dt = K_3.(a-x).(b-x).(c+x)$$

where $(a-x)$ and $(b-x)$ represent the concentrations of silver nitrate and sodium brompropionate respectively and $(c+x)$ the amount of silver bromide in suspension, at any given instant, expressed in terms of molecules of the substance per litre. On integrating the above expression we get

$$K_3 = \frac{2\cdot 3\left((b-a) \times \log \frac{c+x}{x} + (b+c) \log \frac{a}{(a-x)} - (a+c) \log \frac{b}{(b-x)}\right)}{t\cdot \quad (a+c) \quad (b+c) \quad (b-a)}$$

The figures in column 6 of the Tables IV–VII are obtained by calculating the constants in accordance with the above equation. The constancy of K_3 in each of the tables provides ample proof of the general validity of the assumptions made above.

It will be observed that K_3 in different tables has different values. In the more dilute solutions the value of K_3 is greater than in the comparatively more concentrated solutions.

Further experiments were carried out with the object of elucidating, how, at great dilutions, where the reaction proceeds rather slowly (*e.g.*, Table VII), the initial formation of some silver bromide in suspension at the time of the addition of silver nitrate to the reaction mixture would affect the reaction rate. The procedure adopted in the following experiments was as follows:—

To the brompropionate solution contained in a measuring flask (in which the reaction mixture was prepared so as to adjust the concentrations at the desired value by starting with known amounts of more concentrated solutions and subsequent dilution) any desired amount of a standard solution of potassium bromide solution was added and the mixture diluted leaving enough of room for the addition of silver nitrate. An amount of silver nitrate required for the reaction proper and for reacting with potassium bromide was next added, the mixture being kept continuously shaken during the course of the addition. The mixture was finally made upto the mark by the addition of water. The silver bromide was thus formed in the reaction mixture itself in the presence of excess of silver nitrate. The results of these experiments are shown in Tables VIII to XI. The initial concentrations of the reactants in these experiments were

Silver nitrate .. .. 0·001 N
Sodium brompropionate 0·0015 N

The initial amounts of silver bromide present in the different experiments are indicated in the tables. 50 c.c. of the reaction mixture was titrated in each case against N/200 thiosulphate solution.

The concentrations of the reactants in the four experiments were the same as in the experiment the results of which appear in Table VII. It

TABLE VIII.

Silver bromide initially present 0·00050 *mols. per litre.*

Time in minutes	$(a-x)$	$(b-x)$	$(c+x)$	K_3
0	8·80	13·80	6·20	
3	7·50	12·50	7·50	$5·052 \times 10^4$
8	6·15	11·15	8·85	4·46 „ „
13	4·90	9·90	10·10	4·50 „ „
18	4·15	9·15	10·85	4·18 „ „
23	3·10	8·10	11·90	4·56 „ „
30	2·40	7·40	12·60	4·40 „ „
40	1·40	6·40	13·60	4·79 „ „
				4·56 „ „ mean value

TABLE IX.

Silver bromide initially present 0·00075 *mols. per litre.*

Time in minutes	$(a-x)$	$(b-x)$	$(c+x)$	K_3
0	9·00	14·00	8·50	
4	7·15	12·15	10·35	$4·71 \times 10^4$
8	5·60	10·60	11·90	4·80 ,, ,,
12	4·55	9·55	12·95	4·60 ,, ,,
16	3·65	8·65	13·85	4·59 ,, ,,
21	3·00	8·00	14·50	4·30 ,, ,,
27	2·25	7·25	15·25	4·30 ,, ,,
35	1·50	6·50	16·00	4·40 ,, ,,
				4·60 ,, ,, mean value

TABLE X.

Silver bromide initially present 0·0010 *mols. per litre.*

Time in minutes	$(a-x)$	$(b-x)$	$(c+x)$	K_3
0	8·40	13·40	11·60	
3	6·60	11·60	13·40	$5·155 \times 10^4$
7	5·10	10·10	14·90	4·600 ,, ,,
11	4·00	9·00	16·00	4·44 ,, ,,
15	3·30	8·30	16·70	4·14 ,, ,,
20	2·55	7·55	17·45	4·07 ,, ,,
30	1·60	6·60	18·40	3·94 ,, ,,
				4·40 ,, ,, mean value

will be seen that while no silver bromide was initially added to the mixture, six to seven hours are required to enable two-thirds of the silver nitrate to

TABLE XI.

Silver bromide initially present 0·0015 *mols. per litre.*

Time in minutes	$(a-x)$	$(b-x)$	$(c+x)$	K_3
0	7·55	12·55	17·45	
3	5·70	10·70	19·30	$4·45 \times 10^4$
7	4·15	9·15	20·85	4·20 ,, ,,
11	3·05	8·05	21·95	4·16 ,, ,,
15	2·35	7·35	22·65	4·10 ,, ,,
19	1·90	6·90	23·10	3·91 ,, ,,
25	1·35	6·35	23·65	3·90 ,, ,,
				4·12 ,, ,, mean value

react, the presence of 0·0005 mol. of silver bromide in the reaction mixture at the start of the reaction enables the reaction to go to completion in less than an hour.

It is also noteworthy that in spite of the wide variation in the initial amounts of silver bromide in suspension in these different experiments the value of the velocity constant K_3 in all these cases is sensibly the same. These experiments were repeated very carefully and it was found that the results could be very easily reproduced correct to within 2–3 per cent. The term $(c + x)$ is introduced into the velocity expression on the assumption—a very arbitrary assumption at the outset—that the surface offered for reaction is proportional to the amount of silver bromide present in the suspension at any instant. It is remarkable that the constancy of K_3 in these different experiments should so amply justify this assumption. It appears quite justifiable to infer from these data that the silver bromide particles formed in these reaction mixtures are probably of such sizes and shapes that their surface areas are proportional to their masses.

From the standpoint of the kinetics of heterogeneous reactions, since we find, in these dilute solutions, that the velocity of reaction is proportional to the concentration of each one of the reactants raised to the power of one, we infer that the reacting ions are both sparsely adsorbed on the surface of the catalyst.

Experiments were next carried out to see the influence of varying the concentrations of the reactants on the velocity coefficient, when in all the different cases the same amount of silver bromide is generated at the start of the reaction. The results of these experiments are summarised in Table XII. In each one of these experiments very steady constants were obtained almost upto the end of the reaction.

TABLE XII.

Silver bromide initially present in the reaction mixtures 0·0010 *mols. per litre.*

Conc. of brom-propionate	Conc. of silver nitrate	K_3
0·0015 N	0·0005 N	$5{\cdot}7 \times 10^4$
do.	0·0010 N	4·4 „ „
do.	0·0020 N	2·94 „ „
do.	0·0030 N	2·30 „ „
do.	0·0040 N	1·95 „ „
0·00075 N	do.	2·72 „ „
do.	0·0010 N	4·75 „ „
0·00015 N	do.	4·40 „ „
0·0020 N	do.	4·00 „ „
0·0030 N	do.	3·45 „ „
0·0040 N	do.	3·20 „ „
0·0060 N	do.	2·86 „ „

A survey of these data shows that when the concentration of one of the reactants is kept constant and that of the other increased K_3 gradually diminishes in value. Since under all these circumstances, the reaction rate is always found to be proportional to the concentration of each one of the reactants raised to the first power, there can be no doubt that even when the concentrations are varied over the wide range indicated in Table XII, the surface of the catalyst must be only sparsely covered by the reactants in these different cases. The reaction takes place between the two kinds of ions in the adsorbed layer and it can take place only when the two

reacting ions happen to be situated in each other's immediate neighbourhood Consequently, if the concentration of one of these ions happens to be constant in the adsorbed layer while that of the other is increased, the fraction of the total number of ions undergoing chemical change need not necessarily be the same unless the fraction of suitably oriented ions of the two kinds varies commensurately with the increase in the surface concentration of either of the ions. It appears from the data in Table XII that as the ratio between the concentrations of the two kinds of ions in the homogeneous phase (and consequently on the catalyst surface) becomes greater, the relative orientation of the two kinds of ions on the surface becomes less and less favourable for reaction.

Summary and Conclusions.

A detailed study of the kinetics of the reaction between α brompropionate and silver ions has been made in very dilute solutions at 27°C.

The hydrolysis of the brompropionate ion in pure aqueous solutions is an extremely slow reaction. In very dilute solutions (below about 0·001 N) the reaction is an extremely slow one even when silver nitrate solution is added. The velocity of reaction becomes rapid only when some silver bromide is formed in suspension and an analysis of the data obtained in the investigation proves beyond all doubt that the reaction is almost entirely heterogeneous, taking place on the surface of silver bromide particles. In dilute solutions in which silver bromide exists in fine and stable suspension, it has been found that the velocity of reaction is strictly proportional to the amount of silver bromide in suspension.

It is inferred from the order of the reaction that both silver and brompropionate ions are sparsely adsorbed on the surface of the silver bromide particles.

In different experiments, when the initial concentration of one of the reactants is kept constant and that of the other increased, the amount of silver bromide in the different reaction mixtures at the beginning and end of the reaction being nearly the same, it has been found that the velocity constant gradually falls. This variation seems to indicate that as the ratio of the concentrations of the reactants increases under otherwise identical experimental conditions the relative orientation of the two kinds of ions in the adsorbed layer becomes less and less favourable for reaction.

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MAGNETIC BIREFRINGENCE IN SOLUTIONS OF ORGANIC SUBSTANCES, PART I.

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1. *Introduction.*

Extensive measurements have recently been made by Krishnan, Banerjee, Guha and others[1] on the principal magnetic susceptibilities of organic crystals. Their results, taken together with the structure and orientations of the molecules in the crystal lattice obtained from X-ray analysis by Robertson and others,[2] give us definite information regarding the principal susceptibilities of the individual molecules. Since the differences between these principal susceptibilities (*i.e.*, the magnetic anisotropy of the molecules) play an important part in the double refraction produced by a magnetic field on these substances in the liquid state, or in a state of solution in suitable inactive solvents, a detailed study of the latter effect for these compounds would be of interest. As most of them have a high melting point, it was found more convenient to study them in solution rather than in the molten state. We propose in a series of papers, of which this is the first, to give an account of these studies, and to correlate the results with the known structure of the molecules and their magnetic and optical anisotropies. The present part deals with aromatic hydrocarbons containing two or more benzene rings. Similar studies have already been made for some organic substances by M. Ramanadham[3] in this laboratory.

2. *Experimental Method.*

The experimental method adopted was the same as that employed by the author in his recent investigations on the magnetic birefringence of liquid mixtures.[4] The birefringence induced in the solution by the magnetic field was measured with the help of a Rayleigh bent glass compensator, by finding the shift of the central dark band, and comparing it with the shift,

[1] *Phil. Trans. Roy. Soc.*, A, 1933, **231**, 235; 1935, **234**, 265.
[2] Numerous papers in *Proc. Roy. Soc.*, A, 1930–35.
[3] *Ind. Jour. Phys.*, 1929, **4**, 109.
[4] *Ind. Jour. Phys.*, 1933, **7**, 491.

under the same conditions, for a liquid of known birefringence. Carbon bisulphide was found to be a convenient standard for this purpose.

Among the substances studied, anthracene, phenanthrene, fluorene and benzil were from Kahlbaum, pyrene and dibenzyl from Schuchardt, *m*-diphenyl benzene and *s*-triphenyl benzene from Kodak, and the rest from Merck.

3. Results.

The results are given in Table I. Carbon tetrachloride, which has no detectable double refraction, was generally used as the solvent. When the substance was only sparingly soluble in this liquid, other solvents had naturally to be used, and the observed birefringence had to be corrected for that of the solvent. The values given in the table are the corrected ones. They are all expressed in terms of the usual standard of birefringence, *viz.*, that of nitrobenzene = 100.

For convenience of comparison, the birefringence data for the various solutions have been reduced to a uniform standard concentration, namely, 1 gram molecule of the substance per c.c. of the solution.

TABLE I.

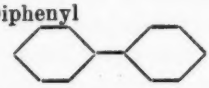
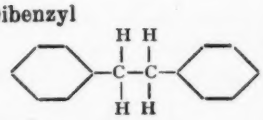
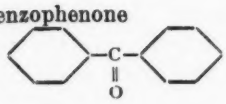
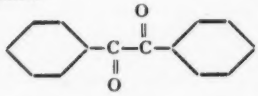
Substance	Solvent	Concentration		Birefringence relative to that of nitrobenzene = 100	
		in gms. per c.c. $\times 10^2$	in gm. moles per c.c. $\times 10^4$	for the actual solution C_m	per gm. mole per c.c. $C_M \times 10^{-2}$
1. Diphenyl 	CCl_4	4·04	2·62	2·3	88
2. Dibenzyl 	,,	8·66	4·75	3·6	76
3. Benzophenone 	,,	8·84	4·86	4·5	93
4. Benzil 	,,	5·38	2·56	2·0	78

TABLE I—(*Contd.*)

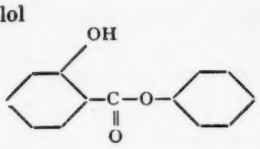
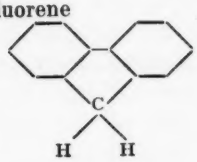
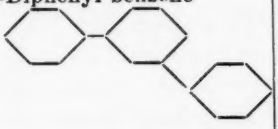
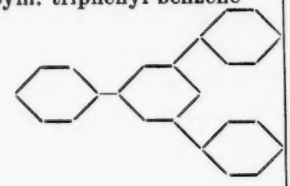
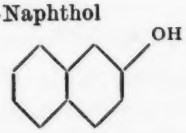
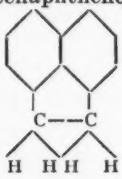
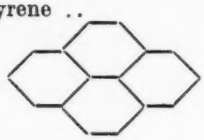
Substance	Solvent	Concentration		Birefringence relative to that of nitrobenzene = 100	
		in gms. per c.c. $\times 10^2$	in gm. moles per c.c. $\times 10^4$	for the actual solution C_m	per gm. mole per c.c. $C_M \times 10^{-2}$
5. Salol 	CCl_4	10·00	4·67	3·3	71
6. Fluorene 	,,	3·33	2·01	3·4	169
	,,	5·07	3·05	5·6	188
7. *m*-Diphenyl benzene 	,,	4·54	1·97	3·25	165
	,,	9·00	3·91	6·9	176
8. Sym. triphenyl benzene 	,,	2·43	0·80	2·35	297
9. Naphthalene	,,	10·08	7·87	10·4	132
10. β-Naphthol 	C_2H_5OH	5·79	4·02	5·1	127

TABLE I— (*Contd.*)

Substance	Solvent	Concentration		Birefringence relative to that of nitrobenzene = 100	
		in gms. per c.c. $\times 10^2$	in gm. moles per c c. $\times 10^4$	for the actual solution C_m	per gm. mole per c.c. $C_M \times 10^{-2}$
11. Acenaphthene 	CCl_4	4·20	2·73	3·3	126
12. Anthracene	Ethyl ether	0·836	0·469	1·75	~370
13. Phenanthrene	CCl_4	4·52	2·54	5·7	224
	,,	8·42	4·73	11·4	243
	,,	10·82	6·07	15·9	261
14. Pyrene .. 	Ethyl acetate	5·44	2·69	10·2	380
15. Benzene	—	88	113	23·3	20·7

4. Discussion of Results.

For a solution in an inactive solvent like CCl_4, the magnetic birefringence is given by the expression

$$C_m = \frac{\pi\nu(\mu^2+2)^2}{135\mu\lambda kT}\left\{(a_1-a_2)(b_1-b_2)+(a_2-a_3)(b_2-b_3)+(a_3-a_1)(b_3-b_1)\right\}, \quad \cdots \quad (1)$$

where a_1, a_2, a_3 are the principal magnetic susceptibilities of the molecule, and b_1, b_2, b_3 are its optical polarisabilities along the three magnetic axes, μ is the refractive index of the solution, ν is the number of molecules of

the *solute* per c.c. of the solution, λ is the wave-length of the incident light, k is the Boltzmann constant, and T is the absolute temperature.

The gram molecular birefringence, given in the last column of Table I, would correspond to the expression

$$C_M = C_m \times N/\nu, \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2)$$

where N is the Avogadro number.

(*a*) *Influence of concentration.*—For dilute solutions, the factor $(\mu^2+2)^2/\mu$ in (1) will vary only very slightly with concentration; we should therefore expect the molecular birefringence C_M to be practically independent of the concentration.

Since most of the substances are only sparingly soluble, and even with the saturation concentration the birefringence is small, it was not possible experimentally to investigate in general the influence of concentration. From the results obtained with the few substances like fluorene, phenanthrene and *m*-diphenyl benzene, which were studied at different concentrations, it appears that the molecular birefringence increases slightly with the concentration, indeed more than can be attributed to the increase in the refractive index factor in (1). The reason for this increase is not clear.

(*b*) *Molecules containing two or more non-condensed benzene rings.*—Let us first consider the simplest of these compounds, *viz.*, diphenyl. Recent X-ray studies by Dhar[5] on the structure of this molecule in the crystal state show that the two benzene rings lie in the same plane, with their centres along the line joining the carbon atoms 1 and 1′, and the principal magnetic susceptibilities of the molecule will, therefore, be nearly double those for benzene, as also the optical polarisabilities. We should therefore expect the molecular birefringence of diphenyl to be nearly 4 times that of benzene. This is actually the case.

In the same manner, for a molecule containing n uncondensed benzene rings, *all lying in the same plane, or in parallel planes,* we should expect the molecular birefringence to be nearly n^2 times that of benzene. If the benzene planes are inclined to one another, the birefringence would naturally be smaller. That for all the substances listed in the following table, except perhaps salol, the magnitude of the birefringence relative to benzene = 1 is nearly of the order of n^2, suggests that in all these molecules the benzene rings, to a first approximation, are either coplanar or are parallel to one another.

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[5] *Ind. Jour. Phys.*, 1932, **7**, 43.

TABLE II.

	Benzene	Diphenyl	Dibenzyl	Benzo-phenone	Benzil	Salol	*m*-diphenyl benzene	Sym-Triphenyl benzene
C_M ..	20·7	88	76	93	78	71	176	297
C_M relative to benzene	1	4·2	3·7	4·5	3·8	3·4	8·5	14·3
n^2 ..	1	4	4	4	4	4	9	16

(*c*) *Fluorene.*—For fluorene, however, the birefringence is considerably higher than that for the two-ringed compounds considered above, and this is to be attributed to the presence of the extra five-membered ring, and to the condensed nature of the rings, which, as we shall see, conduces to a large magnetic and optical anisotropy.

(*d*) *Molecules containing condensed benzene rings.*—We have seen that as we go from benzene to diphenyl, the principal magnetic susceptibilities, both in the plane of the benzene rings, and along the normal to the plane, are nearly doubled. On the other hand, when the two rings are fused together, as in naphthalene, though the susceptibility along the normal to the plane of the molecule is nearly twice that due to a single benzene ring, that in the plane of the naphthalene ring is not much higher than that of a single ring. Denoting the two principal susceptibilities of the molecule in the plane of the benzene rings by a_1 and a_2, and that along the normal to the plane by a_3, their values for some of the simple molecules, taken from Krishnan and Banerjee's paper,[6] are given in the following table.

While for molecules containing uncondensed benzene rings, *e.g.*, diphenyl, diphenylbenzene and triphenylbenzene, the value of $a_1 - a_3$ is nearly n times that of the benzene molecule; for naphthalene and anthracene, in which the benzene rings are condensed, the value of $a_1 - a_3$ is much higher than for a molecule containing the same number of uncondensed rings. In phenanthrene and pyrene, however, the influence of the condensation on the magnetic anisotropy $a_1 - a_3$ is not so marked.

We can now utilise the magnetic birefringence data to find also how the *optical* anisotropy of the molecule is affected by the condensation of the

[6] See ref. 1.

TABLE III.

Molecule	Principal magnetic susceptibilities of the molecules			β
	$-a_1 \times N \times 10^6$	$-a_2 \times N \times 10^6$	$-a_3 \times N \times 10^6$	
Benzene	37	37	91	1·0
Diphenyl	67	67	175	2·1
Naphthalene	39	43	187	2·4
Anthracene	46	53	273	4·3
Phenanthrene ..	74	74	240	3·6
Pyrene	81	81	303	4·5

benzene rings. For the above molecules, since $a_1 = a_2$, the anisotropies factor in expression (1) reduces to the simple form

$$(a_1 - a_3)\ (b_1 + b_2 - 2b_3).$$

The values of $(b_1 + b_2 - 2b_3) = \beta$, say, for the different molecules, in terms of the corresponding value for the benzene molecule as unity, are given in the last column of Table III.

It will be seen that for the condensed molecules the values in the last column are higher than n, the number of benzene rings, showing that the condensation of the rings conduces to an increase in the optical anisotropy also, as we should expect.

5. *Summary.*

A number of aromatic hydrocarbons containing two or more benzene rings have been studied for their magnetic birefringence in solution in suitable solvents. For diphenyl and most of its simple derivatives the molecular magnetic birefringence is nearly 4 times, for *m*-diphenylbenzene containing 3 benzene rings, it is 9 times, and for triphenyl benzene nearly 14 ($\sim 4^2$) times, that of benzene, suggesting that the benzene rings in these molecules are, to a first approximation, either coplaner or parallel to one another.

When the benzene rings are "condensed", the magnetic and optical anisotropies are found to be much higher than when they are separate.

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By Max Born.

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1. Introduction.

Modern physics is dominated by two fundamental principles, Einstein's theory of relativity and Planck's quantum theory. Both theories are generalisations of the classical laws of mechanics and electrodynamics. Relativity deals with the influence of relative motions on the physical phenomena; the classical laws refer to the limiting case of slow velocities, slow compared with the velocity of light, $c = 3 \times 10^{10}$ cm./sec., and new effects, as for instance the variability of mass with velocity, are only measurable if the velocity of the particle observed approaches c. Quantum theory, on the other hand, has to do with the finest structure of light and of matter; the classical laws are the limiting case for matter in bulk. There exists a certain number of the dimension energy $\times$ time or "action", Planck's constant $h = 6{\cdot}5 \times 10^{-27}$ erg./sec. which is characteristic for quantum phenomena; these appear whenever an "action" is of the order of h or smaller. Both theories are developed to a high degree of perfection. But they are not melted into a unit. Quantum theory is a wonderful mathematical structure and predicts the natural phenomena with amazing success, as long as the velocities of the particles involved are small compared with the velocity of light, *i.e.*, as long as relativity effects can be neglected. Fortunately, this restriction is fulfilled in many problems which atomic physics has to deal with. The velocities of the electrons forming the outer parts of atoms are generally small compared with c. Even in nuclear physics the motion of protons and neutrons, due to their great mass (1840 times that of the electron), are slow enough to neglect relativity corrections. This fact is made use of in the newest attempts to devise theoretical pictures of nuclear structure with the help of quantum mechanics. But there are phenomena where fast particles are involved and the non-relativistic quantum theory breaks down. The first effect of this kind was studied by Sommerfeld in 1916, the fine structure of the spectral lines of Hydrogen. He discovered that in the law of this splitting there appears a dimensionless combination of the fundamental physical constants, the velocity of light c, the quantum

constant h and the electronic charge e. This fine structure constant is the mysterious number referred to in the title of this lecture. The importance of this number extends far beyond the special problem where it was discovered. The aim of this lecture is to show that all finer laws of atomic physics are governed by this number, and to explain some ideas about its deeper meaning.

2. *Bohr's Orbits.*

As Sommerfeld's work was based on the older quantum theory of Niels Bohr, we have to start with a short recapitulation of this theory.

We consider a system consisting of a nucleus with the positive charge eZ, and an electron with the negative charge $-e$, where e is the elementary charge of electricity, $e = 4{\cdot}77 \times 10^{-10}$ e.s.u.

Since the force acting between these particles corresponding to Coulomb's law is $-\frac{e^2Z}{r^2}$, where r is the distance, they move in Keplerian ellipses around their centre of gravity. The energy of this motion does not depend on the eccentricity of the ellipse, but only on the major semi-axis a; if we take as zero-point of the energy E the state where the electron is detached from the nucleus and at rest, E is negative and has the value

$$\mathrm{E} = -\frac{Ze^2}{2a}.$$

Kepler's third law connects a with the time T of revolution or its reciprocal, $\nu = \frac{1}{\mathrm{T}}$, the number of revolutions per unit time:

$$\frac{a^3}{\mathrm{T}^2} = a^3\nu^2 = \frac{Ze^2}{4\pi^2 m}.$$

Here m can be taken as the mass of the electron since the heavy nucleus can be considered as practically at rest. (The influence of the nuclear motion, important for other phenomena, but small, will not be discussed here.)

These classical laws of motion would permit the energy E adopting values over a continuous range. Bohr assumes that only a discrete set of values of E are really permissible, by applying Planck's quantum theory to this system. The simplest way of doing this is by using the quantum principle that the angular momentum of a rotating system always has to be an integral multiple of $\frac{h}{2\pi} = \hbar$; the latter symbol, introduced by Dirac, will be used here throughout. For a circular orbit of radius a, circumference $2\pi a$, the velocity is $\frac{2\pi a}{\mathrm{T}} = 2\pi a\nu$, the momentum $2\pi a\nu m$, the angular momentum $2\pi a\nu m \times a = 2\pi\nu m a^2$. Hence the quantum condition is

$$2\pi\nu m a^2 = \hbar n, \quad n = 1, 2, 3, \ldots\ldots\ldots\ldots$$

From the last three equations we get

$$a = \frac{\hbar^2}{me^2} \cdot \frac{n^2}{Z}, \qquad E = -\frac{me^4}{2\hbar} \cdot \frac{Z^2}{n^2}.$$

These expressions hold also for elliptic orbits with the major semi-axis a.

We have developed these well-known formulæ because the combinations of constants appearing here have a far-reaching importance. We shall denote them by

$$a_1 = \frac{\hbar^2}{me^2} = 0{\cdot}532 \times 10^{-8} \text{ cm.},$$

$$E_1 = \frac{me^4}{2\hbar} = 2{\cdot}15 \times 10^{-11} \text{ erg.}$$

Then the stationary states of the H-atom and similar one-electron systems are given by

$$a_n = a_1 \frac{n^2}{Z}, \quad E_n = -E_1 \frac{Z^2}{n^2};$$

a_1 and E_1 are the radius and energy of the first orbit of the H-atom ($Z = 1$).

E_n is called " Balmer term " ; for if we apply Bohr's frequency condition for the light emitted or absorbed,

$$h\nu = E - E'$$

to the case of one H-atom, we get

$$h\nu = E_1 \left(\frac{1}{n'^2} - \frac{1}{n^2} \right)$$

and this formula represents in fact for $n' = 2$, $n = 3, 4, 5, \ldots$. the Balmer series of hydrogen. For other values of n' we get all other known series of this atom, and for $Z = 2, 3, \ldots$. the corresponding series of the one-electron ions He^+, $Li^{++}, \ldots$.

A closer examination of these lines has shown that they are not simple, but have a fine structure ; the examination of this is the problem which Sommerfeld has attacked. But before we talk about this refinement, we have to consider the physical importance of the two constants a_1 and E_1, introduced by Bohr.

3. *Atomic Units.*

Bohr's orbits, based on a combination of classical mechanics and quantum conditions, are logically unsatisfactory and have been replaced by more abstract theories, quantum mechanics in its different forms. But the fundamental constants a_1 and E_1, introduced by Bohr, have not been replaced, but are the natural units of length and energy for all atoms, as long as the velocities of the electrons are small compared with c. As Hartree has shown, the properties of all atoms expressed in these " *atomic units* " a_1, E_1 are pure

mathematical numbers or functions. The Hamiltonian of an atom, *i.e.*, its energy as function of the momenta $\vec{p}_1, \vec{p}_2, \ldots$ and coordinates $x_1, y_1, z_1, x_2, y_2, z_2, \ldots$ of the electrons, is

$$\mathrm{H} = \frac{1}{2m} \sum_k p_k^2 - \sum_k \frac{Ze^2}{r_k} + \sum'_{k,l} \frac{e^2}{r_{kl}},$$

where r_k is the distance of the kth electron from the nucleus, r_{kl} the mutual distance of the kth and the lth electron. The atom is described by Schrödinger's wave equation $(\mathrm{H} - \mathrm{E})\psi = 0$, where H is the differential operator constructed by replacing the components of $\vec{p}_k$ by

$$\frac{\hbar}{i}\frac{\partial}{\partial x_k}, \quad \frac{\hbar}{i}\frac{\partial}{\partial y_k}, \quad \frac{\hbar}{i}\frac{\partial}{\partial z_k}.$$

Now it is easily seen that by introducing a_1 and E_1 as units, the wave equation becomes

$$\left\{ -\tfrac{1}{2}\sum_k \left(\frac{\partial^2}{\partial x_k^2} + \frac{\partial^2}{\partial y_k^2} + \frac{\partial^2}{\partial z_k^2} \right) - \sum_k \frac{Z}{r_k} + \sum'_{k,l} \frac{1}{r_{kl}} - \frac{1}{2}\mathrm{E} \right\} \psi = 0.$$

It contains only numerical constants. If the number of the electrons is 1 we get the wave equation of the H-atom ; the energies of the stationary states turn out to be exactly given by the Balmer term, which in atomic units is

$$\mathrm{E}_n = -\frac{Z^2}{n^2}.$$

But in the same way the geometric dimensions and energies of all the atoms are dimensionless mathematical numbers when expressed in atomic units.

The same holds for molecules, if the motions of the nuclei are neglected. This is permitted, since the masses of the nuclei are very large compared with the mass of the electron. After having chosen an arbitrary position of the nuclei we can determine the electronic motion by a Schrödinger equation, which in atomic units contains no other constants (besides mathematical numbers) than the coordinates of the nuclei. The energy of the electrons is then a function of these nuclear coordinates, $\mathrm{E}(\mathrm{X}_1, \mathrm{Y}_1, \mathrm{Z}_1, \mathrm{X}_2, \mathrm{Y}_2, \mathrm{Z}_2, \ldots)$ and its minima determine the possible configurations of the nuclei. If $\mathrm{X}_1, \mathrm{Y}_1, \mathrm{Z}_1, \mathrm{X}_2, \ldots\ldots$ are expressed in atomic units, it is evident that the relative positions of the nuclei in the molecule are given by purely mathematical numbers. That means that all molecules have dimensions of the order a_1 and energies of the order E_1. Crystals are nothing but very big molecules. If the number of atoms is given, the dimensions and energies of a crystal formed by them at low temperatures are determined by the order of magnitude of a_1 and E_1.

There are many collision processes which belong to the same class of phenomena governed by a_1, E_1, namely all those where the motion of the

nuclei can be neglected and the velocity of the electrons is small compared with c, *i.e.*, excitation and ionisation of atoms or molecules by slow electrons. The effective cross-section and the angular distribution of these processes can be calculated from the same wave equations as the stationary states; they are purely mathematical numbers, when the units a_1, E_1 are chosen.

We see that a great field of physics is governed by the atomic units a_1, E_1. But there are many cases where these do not suffice.

The first rather trivial exception refers to the motion of the nuclei. Whenever these play a rôle, in the heat motion of gases or solids, in optical effects, the nuclear masses are a determining factor.

Empirically these masses are given by the "atomic weights". But we know from Aston's experiments with the mass spectrograph, that the chemically measured atomic weights do not belong to pure substances but to mixtures of isotopes, *i.e.*, nuclei with the same charge Ze, but different masses. The masses of pure isotopes are nearly exact multiples of the smallest M, that of the H-nucleus, or proton. The small deviations found from these integer values (in units M) are easily explained by the assumption that the higher nuclei are not simple additions of protons, but held together by some binding energies. As energy, corresponding to Einstein's law, means mass, the energy liberated in combining protons to nuclei results in a diminution of mass. Therefore the only new physical constant introduced by the consideration of the nuclei is the mass M of the proton which is about 1840 times that of the electron. This number, the mass quotient $\frac{M}{m} = 1840$ is a second mysterious number of physics. It determines the order of magnitude of all nuclear motions, for instance velocities of gas molecules, rotations and vibrations of these, vibrations of crystal lattices and all properties of matter depending on these motions: specific heat, thermal conductivity, diffusion, infra-red absorption, Raman effect, chemical reaction velocities, etc.

But I believe that the problem of the number 1840 is closely connected with that of the number 137 which is the proper subject of this lecture. We shall return to this point later.

4. Sommerfeld's Fine Structure Formula.

We come now to the second limitation of the application of the atomic units a_1, E_1, namely, the assumption that the velocities of the electrons are small compared with c. Whenever this fails to be true, we have to take relativity into account.

This was first done by Sommerfeld for the explanation of the fine structure of the hydrogen lines. As mentioned, he developed his formula from the standpoint of Bohr's orbit; this method shows clearly the point where the relativity effect becomes important. Therefore we shall start with a short report on Sommerfeld's considerations. We have mentioned that all elliptical orbits of the same major axis have the same energy irrespective of their eccentricity. But for very eccentric orbits the perihelion gets very close to the nucleus and the velocity in its neighbourhood becomes very high. Then the classical laws of mechanics cease to be valid and have to be replaced by relativity mechanics. This means that the mass is no longer constant, but increases with the velocity. If this is taken into account the motion is no longer an ellipse with fixed axis but a rosette motion which can be described as the superposition of the classical elliptical motion and a precession of the perihelion. The period of this precession depends on the degree of eccentricity and has to be quantised with the help of a new quantum number k, which can assume all values 0, 1, 2,..... The energy becomes a function of k which in the first approximation is given by

$$E = - E_1 \frac{1}{n^2}\left\{1 + \left(\frac{e^2}{\hbar c}\right)^2 Z^2 \left[\frac{n}{k} - \frac{3}{4}\right]\right\}.$$

This formula represents many more stationary states, as to each value n there belong several states with different k. Therefore each spectral line is split up into a set of lines.

The experimental confirmation of the fine structure formula of Sommerfeld is considered as a brilliant proof, simultaneously of Einstein's principle of relativity and Planck's quantum theory.

Here we have the first attempt to unite these two great ideas. As we have remarked they are characterised each by a universal constant, relativity by c, quantum theory by $\hbar$. It is natural that in Sommerfeld's formula, the correction term depends on both these quantities, the coefficient being the square of the quantity

$$\alpha = \frac{e^2}{\hbar c}$$

which Sommerfeld has called fine structure constant.

This constant is the reciprocal of the mystical number 137 which I have chosen as the title of this lecture. Why is there anything mystical about it? and why is it worth while to speak about it?

The astonishing point is that this combination α of three universal constants of nature is a dimensionless number. One can see this at once.

The electrical force between two particles with equal charges e in the distance r is corresponding to Coulomb's law given by $\frac{e^2}{r^2}$; the energy necessary to separate them, by $\frac{e^2}{r}$. Therefore e^2 can be measured as erg × cm. The units of $\hbar$ are erg × sec. those of c are cm./sec. ; $\hbar c$ is therefore measured in erg × sec. × cm./sec. or erg × cm., it has the same dimensions as e^2. Introducing the known values of e, $\hbar$, c, one finds

$$\alpha = 0{\cdot}00734, \text{ or very nearly } = \frac{1}{137}.$$

The fact that this number is small compared with 1, is not only the justification for considering the relativity effect as small (its influence as a fine structure), but has the most fundamental consequences for the structure of matter in general.

The mystery referred to in the title becomes apparent when we compare the two numerical coefficients in the fine structure formula

$$E = -E_1 \frac{1}{n^2}\left\{1 + \left(\frac{1}{137}\right)^2 Z^2 \left[\frac{n}{k} - \frac{3}{4}\right]\right\},$$

namely $(^1/_{137})^2$ and $\frac{3}{4}$. The latter is an arithmetical expression derived by mathematical reasoning. The other factor is not of this character. It was found as a combination of physical quantities with dimensions, measured in arbitrary units, and our knowledge of its value depends on the accuracy of these measurements.

Is this state of affairs satisfactory ? I think not in the least. We should expect that numerical coefficients in physical laws are always mathematical numbers like $\frac{3}{4}$ or π or something of the kind. If this here seems to be different it must mean an incompleteness of the theory. A perfect theory should be able to derive the number α by purely mathematical reasoning without recourse to experience. But then we are led to a remarkable conclusion : If α is a mathematical number, the constants e, $\hbar$, c are not independent ! In other words, from measurements of two of them the third can be calculated. Assuming for instance $\hbar$ and c as primary quantities, the complete theory should permit to calculate the charge of the electron ! But speculating about a future theory is rather awkward, and before we say something about this question, we have to consider the rôle which the number 137 plays in the existing theory.

5. *Electronic Units.*

We have seen that the non-relativistic properties of all atoms and molecules can be expressed by pure mathematical numbers, using Hartree's atomic units a_1, E_1 for length and energy. Sommerfeld's results show that

these do not suffice for all properties of the atoms, the relativistic effects depending on the constant α. Now a_1 and E_1 are composed of properties of the electron, e and m, and of the quantum constant $\hbar$. The latter appears also in α, and as this has a numerical value, one can eliminate $\hbar$ from the expressions a_1, E_1:

$$a_1 = \frac{\hbar^2}{me^2} = \frac{e^2}{mc^2}\left(\frac{\hbar c}{e^2}\right)^2 = \frac{e^2}{mc^2}\frac{1}{\alpha^2} = (137)^2\frac{e^2}{mc^2},$$

$$E_1 = \frac{me^4}{2\hbar^2} = \frac{1}{2}mc^2\left(\frac{e^2}{\hbar c}\right)^2 = \frac{1}{2}mc^2\,\alpha^2 = \frac{1}{2}\frac{1}{(137)^2}mc^2.$$

Now a_1, E_1 are expressed by properties of the electron alone, a length, $a_0 = \frac{e^2}{mc^2}$, and an energy, $\epsilon = mc^2$. What is the meaning of these?

The answer for the energy is given by Einstein's fundamental law which he derived in connection with the theory of relativity, stating that mass and energy are physically identical, their relation being c^2. Therefore

$$\epsilon = mc^2$$

is the *energy of the electron.*

Similarly the length $a_0 = \frac{e^2}{mc^2}$ can be considered as the radius of the electron; but about this point we have to say some words.

To-day most physicists are inclined to consider the electron as a point charge and to ignore any question about its size and form as unanswerable and meaningless. It was not always like that. A quarter of a century ago it was good fashion to consider the electron as a body of finite dimensions, for instance as a sphere of radius a_0 with a charge distributed on its surface or throughout its volume. Then it was possible to derive the electromagnetic energy of the electron, and its electromagnetic momentum p from Maxwell's equations in terms of charge e and radius a_0. The result was for a sphere and for slow velocities of the form

$$\epsilon = A\frac{e^2}{a_0}, \qquad p = B\frac{e^2}{a_0}\frac{v}{c^2},$$

where A and B were numerical coefficients depending on the distribution of charge.

Both expressions become infinite for $a_0 = 0$. The assumption of the electron being a point charge is therefore impossible, as long as Maxwell's equations are accepted as rigorously valid.

The second formula which has the form $p = mv$ suggests very strongly the interpretation of the coefficient $m = B\frac{e^2}{a_0c^2}$ as the electromagnetic mass of the electron.

Corresponding to Einstein's law $mc^2 = \epsilon$ one should expect to have $mc^2 = B\frac{e^2}{a_0}$ equal to $\epsilon = A\frac{e^2}{a_0}$, or $A = B$. But the calculation with the help of Maxwell's equation gave the result that these coefficients are not equal, *e.g.*, for a surface charge $A = \frac{2}{3} B$!

The explanation of this discrepancy was seen in the assumption that the charges were kept together on the sphere representing the electron by some very strong coherence forces of unknown origin; without these forces the electron ought to explode in consequence of the mutual repulsions of its equally charged parts. These forces should contribute to the energy and yield the missing $\frac{1}{3} B$. But this explanation looks rather artificial and unsatisfactory. The geometrical form and the charge distribution are just as arbitrary as those coherence forces. Therefore physicists generally preferred to refrain from any hypothesis on the interior of the electron. But on the other hand the relation between mass or energy of the electron and radius was too beautiful to be given up. Therefore one began to consider the equation

$$\frac{e^2}{a_0} = mc^2 = \epsilon = 8{\cdot}1 \times 10^{-7} \text{ erg},$$

with the arbitrary choice of the coefficient $A = 1$, as *definition* of the conventional *radius a_0 of the electron*:

$$a_0 = \frac{e^2}{mc^2} = 2{\cdot}82 \times 10^{-13} \text{ cm}.$$

It is the length, by which the radius a_1 of the first orbit of the H-atom is expressed; we can write

$$E_1 = \frac{\alpha^2}{2}\epsilon = \frac{\epsilon}{2(137)^2} = \frac{\epsilon}{2 \times 18770},$$

$$a_1 = \frac{1}{\alpha^2} a_0 = (137)^2 a_0 = 18770\, a_0.$$

We realise now the great importance of the number 137, the square of which determines the relation of the energy and radius of the H-atom, E_1 and a_1, to the energy and radius of the electron, ϵ and a_0.

We shall call ϵ, a_0 *electronic units* of energy and length. As $e^2 = a_0 \epsilon$ the value of e in these units is 1.

The large value of $\frac{1}{\alpha^2} = (137)^2 = 18770$ is apparently the justification for treating the electrons in atoms or molecules as point charges with fixed masses. If you enlarge the electron to the size of a pea (diameter $\frac{1}{2}$ cm.) the hydrogen atom would be a sphere with a diameter of 100 m. The binding

energy of the atom is small in the same relation to the self-energy of the electron.

We shall now show that using electronic units all laws of atomic physics become dimensionless equations with numerical coefficients; but these are not all purely mathematical numbers, but amongst them appears the constant α. The great value of $\frac{1}{\alpha} = 137$ is the decisive factor for the order of magnitude of all physical phenomena, when reduced to electronic units.

6. Relativistic Wave Equations.

Sommerfeld's explanation of the fine structure was a most important pioneer work, but suffered from the same insufficiencies as Bohr's theory in general and had to be replaced by the modern methods of quantum mechanics. We have now to consider the attempts to construct a wave equation for the electron which satisfies the principle of relativity.

The first relativistic wave equation for a single electron in a given electromagnetic field has been stated by Gordon and Klein; it reads

$$\left\{ -\left(\frac{W}{c} - \frac{eA_0}{c}\right)^2 + \left(\vec{p} + \frac{e\vec{A}}{c}\right)^2 + m^2c^2 \right\} \psi = 0.$$

Here the operator W means $-\frac{\hbar}{i}\frac{\partial}{\partial t}$, in complete analogy to $p_x = \frac{\hbar}{i}\frac{\partial}{\partial x}$, ...

A_0 is the scalar and $\vec{A}$ the vector potential of the external field. As this field is generated by electrons or nuclei, we can split from the potentials the factor $\frac{e}{a_0}$ representing the potential of the point charge e at the distance a_0:

$$A_0 = \frac{e}{a_0}\phi_0, \qquad \vec{A} = \frac{e}{a_0}\vec{\phi},$$

then ϕ_0, $\vec{\phi}$ are dimensionless functions of space and time. If we take a_0 as unit of length, a_0/c as unit of time, the wave equation becomes:

$$\left\{ -\left(\frac{1}{i}\frac{\partial}{\partial t} - a\phi\right)^2 + \left(\frac{1}{i}\frac{\partial}{\partial x} + a\vec{\phi}\right)^2 + \cdots + a^2 \right\} \psi = 0.$$

It contains only the dimensionless constant a. But this equation fails to represent an important property of the electron, the spin, or the fact that the electron has a mechanical angular momentum half that of the first orbit of Bohr, $\frac{1}{2}\hbar$, and a magnetic moment of the same amount as this orbit, $\frac{e\hbar}{2mc}$. Theoretically there are difficulties in interpreting the equation because of the appearance of the second derivative with respect to time of ψ. The statistical interpretation assumes that $|\psi|^2\ dx\ dy\ dz$ is the probability of finding

the electron in a specified element $dx\,dy\,dz$ of space. But then the knowledge of the distribution function ψ at the time $t = 0$ should suffice to calculate it at any other time; the differential equation ought to be of the first order in t. But since it is of the second order the initial conditions must include the value of $\frac{\partial\psi}{\partial t} = 0$ for $t = 0$, which is difficult to understand.

These considerations led Dirac to his celebrated wave equation of the first order in x, y, z and t:

$$\left\{\left(\frac{\mathrm{W}}{c} + \frac{e}{c}\mathrm{A}_0\right) + \vec{\gamma}\left(\vec{p} + \frac{e}{c}\vec{\mathrm{A}}\right) + \gamma_0 mc\right\}\psi = 0,$$

which contains as coefficients four numerical (dimensionless) operators or matrices $\gamma_0, \vec{\gamma} = (\gamma_1, \gamma_2, \gamma_3)$.

The most important property of Dirac's equation is the fact that it explains the spin of the electron. This becomes evident if one tries to deduce from it the Gordon-Klein equation as a first approximation; then there appear additional terms of the form

$$\frac{\hbar e}{2mc}\vec{\sigma}\vec{\mathrm{H}}$$

where $\vec{\mathrm{H}}$ is the magnetic field strength and $\vec{\sigma}$ a vector-operator, composed of the γ's (and a similar electric term which is imaginary and has no immediate meaning). This can be interpreted as the energy of interaction of the field $\vec{\mathrm{H}}$ and the magnetic moment of the electron having the magnitude $\frac{\hbar e}{2mc}$, called a *magneton*.

If we introduce electronic units, Dirac's equation becomes

$$\left\{\left(\frac{1}{i}\frac{\partial}{\partial t} - a\phi_0\right) + \vec{\gamma}\left(\frac{1}{i}\frac{\partial}{\partial x} + a\vec{\phi}\right) + \gamma_0 a\right\}\psi = 0;$$

it contains only the number $a = \frac{1}{137}$.

The magneton can be written $\frac{\hbar e}{2mc} = \frac{1}{2}e\frac{e^2}{mc^2}\frac{\hbar c}{e^2} = \frac{ea_0}{2a}$, where ea_0 is the electric moment of two elementary charges in the distance a_0, which in electronic units is equal to 1. The magneton is in these units $\frac{1}{2a} = 68{\cdot}5$.

If the potentials do not vary with time there exist stationary states which one gets by taking ψ proportional to $e^{\frac{i}{\hbar}\mathrm{E}t}$, or in the electronic units

$e^{i\alpha Et}$. The wave equation, divided by α, is then

$$\left\{E - \phi_0 + \vec{\gamma}\left(\frac{1}{i\alpha}\frac{\vec{\partial}}{\partial x} + \vec{\phi}\right) + \gamma_0\right\}\psi = 0.$$

In the case of a hydrogen-like atom or ion the field of the nucleus is described by a scalar potential $A_0 = \frac{Ze}{r}$, whereas $\vec{A} = 0$; or in electronic units $\phi_0 = \frac{Z}{r}$, $\vec{\phi} = 0$. The equation can be rigorously solved; the stationary states are given by

$$E = \frac{1}{\sqrt{1 + \frac{\alpha^2 Z^2}{\{n - k + \sqrt{k^2 - \alpha^2 Z^2}\}^2}}}$$

where n, k are the same quantum numbers as in Sommerfeld's theory. As a matter of fact, the same formula has been already derived by Sommerfeld using the old method of Bohr's orbits. One can easily see that the approximate formula given at the beginning of our discussion can be got from the exact one by a development with respect to powers of α. The zero order term is the rest energy of the electron (1 in electronic units) not written in Sommerfeld's formula; the first order term in α^2 corresponds to the Balmer term, the next term to Sommerfeld's fine structure correction.

The complete agreement of the exact formula with the structure of the X-ray spectra up to the highest atomic numbers shows that the number 137 governs the behaviour of a stationary electron in a nuclear field to the finest detail.

7. *Interaction of Electrons and Radiation.*

The most important case where the constant α enters into the laws of physics is the interaction of electrons with electromagnetic radiation.

In the preceding considerations we have dealt with stationary states of the atoms or molecules, their dimensions and energies. But an excited state has a natural instability because the surrounding ether can take energy from the atom and carry it away as radiation or light. This process depends on the constant α, as can easily be seen by a semi-classical consideration.

A vibrating electron of the frequency ν sends out energy in form of electromagnetic waves corresponding to the law

$$-\frac{dE}{dt} = \frac{1}{\tau}E,$$

where the constant τ, of the dimension of a time, is given by

$$\tau = \frac{3}{8\pi^2}\frac{mc^3}{e^2\nu^2}.$$

This classical law of radiation can be transferred to the quantum theory. Then we have not a continuous loss of energy, but instantaneous transitions from excited states to lower states. Each excited state has a certain life time which is unambiguously determined by the wave equation of Schrödinger, with the help of the matrix element of the dipole moment of the system.

The result of this consideration is that all life times are of the form $f\tau$, where τ is the constant given above and f a mathematical number, characteristic for the state considered.

Let us now calculate the life time of the first excited state of the H-atom and compare it with the period of vibration corresponding to the transition to the ground state. In this case f turns out to be nearly 1. Hence the life time is τ, and as the period is $\mathrm{T} = \frac{1}{\nu}$, the ratio in question is

$$\frac{\tau}{\mathrm{T}} = \nu\tau = \frac{3}{8\pi^2}\frac{mc^3}{e^2\nu}.$$

Introducing here for ν the value from Balmer's formula

$$\nu = \frac{1}{h}\mathrm{E}_1\left(\frac{1}{1^2} - \frac{1}{2^2}\right) = \frac{3}{4h}\mathrm{E}_1 = \frac{3}{8h}mc^2\alpha^2,$$

we find easily

$$\frac{\tau}{\mathrm{T}} = \frac{2}{\pi}\frac{1}{\alpha^3} = \frac{2}{\pi}(137)^3 = 1{\cdot}64 \times 10^6.$$

The reciprocal of this is the relative width of the spectral line,

$$\frac{\Delta\nu}{\nu} = 6{\cdot}1 \times 10^{-7}.$$

This quotient can also be considered as the coupling energy of electronic motion and radiation field, $h\,\Delta\nu$ relative to the emitted energy, $h\nu$.

The enormous length of the life time measured in periods of emitted vibrations, or the extreme smallness of the coupling energy between atom and ether is of the greatest importance for the appearance of the physical world and our method to describe it. It makes it possible to separate atoms from the surrounding field and to ascribe to them stationary states. If α were bigger than it really is, we should not be able to distinguish matter from ether, and our task to disentangle the natural laws would be hopelessly difficult. The fact however that α has just its value $\frac{1}{137}$ is certainly no chance but itself a law of nature. It is clear that the explanation of this number must be the central problem of natural philosophy. But before we can discuss this question we have to mention many other phenomena determined by the value of α.

One of the simplest in principle, even simpler than the radiation of a bound electron just considered, is the interaction of free electrons and radiation. This can be treated rigorously with the help of Dirac's equation, by introducing into it the alternating field of a light wave. Then the static potential ϕ_0 vanishes, the vector potential $\vec{\phi}$ is a periodic function of $(\nu t - \vec{k}\,\vec{r})$ representing a wave with the frequency ν and the wave-vector $\vec{k}$ (*i.e.*, a vector in the direction of the wave normal and a length $\frac{1}{\lambda}$, when λ is the wave-length).

The effect of light waves on free electrons consists in a scattering of the light. If the frequency is high, as for X-rays, the scattered wave has a lower frequency as the primary wave. This is the Compton effect. It is well known that it can be explained by an application of the laws of conservation of energy and momentum, ascribing the light quantum the energy $h\nu$ and the momentum $\frac{h\nu}{c}$; the result of a simple calculation is

$$\Delta\lambda = 2\lambda_0 \sin^2 \frac{\phi}{2},$$

where ϕ is the angle of deflexion of the light quantum and λ_0 the socalled Compton wave-length, namely

$$\lambda_0 = \frac{h}{mc} = 2{\cdot}42 \times 10^{-10} \text{ cm}.$$

This length is characteristic for pure quantum effects, just as the electronic radius

$$a_0 = \frac{e^2}{mc^2} = 2{\cdot}82 \times 10^{-13} \text{ cm}.$$

is characteristic for purely electronic effects. Their quotient

$$\frac{a_0}{\lambda_0} = \frac{e^2}{hc} = \frac{1}{2\pi}\frac{e^2}{\hbar c} = \frac{\alpha}{2\pi}$$

is again the fine structure constant, divided by 2π.

The existence of the mysterious number can therefore be ascribed to the fact, that there are two different "natural" units of length, in our laws of nature, a larger one λ_0 taken from quantum theory, a smaller one a_0 taken from the electron.

The probability laws of the scattering of light, the law of angular distribution and the total yield, can be expressed with the help of an effective cross-section q. For long waves this can be deduced from the field equations

of Maxwell and classical mechanics ; the result is J. J. Thomson's well-known formula

$$q = \frac{8\pi}{3} a_0^2.$$

For shorter waves Dirac's equation has to be used ; the calculation, first performed by Klein and Nishina, gives an expression for the cross-section, which deviates from Thomson's formula by a function of $\eta = \frac{\lambda_0}{\lambda}$, where λ is the wave-length of the incident light and $\lambda_0 = \frac{h}{mc}$ the Compton wave-length :

$$q = \frac{8\pi}{3} a_0^2 f(\eta),$$

with

$$f(\eta) = \tfrac{3}{4} \left\{ \frac{1+\eta}{\eta^2} \left[\frac{2(1+\eta)}{1+2\eta} - \frac{1}{\eta} \log (1+2\eta) \right] + \frac{1}{2\eta} \log (1+2\eta) - \frac{1+3\eta}{(1+2\eta)^2} \right\}.$$

Since, as we have seen, $\lambda_0 = \frac{a_0}{\alpha} = 137 a_0$, we have $\eta = \frac{1}{\alpha\lambda}$, when λ is measured in electronic units. Then

$$q = \frac{8\pi}{3} f\left(\frac{1}{\alpha\lambda}\right) = \frac{8\pi}{3} f\left(\frac{137}{\lambda}\right)$$

is a numerical function of λ which contains the constant $\alpha = \frac{1}{137}$.

There are many other possibilities of interaction between light quanta and charged particles. One important case is the scattering of a beam of electrons passing a nucleus with emission of light. It turns out that this process is more effective causing absorption of the electronic beam than any other process (as excitation or ionisation), provided that the energy is high, greater than $\epsilon = mc^2$ (or 1 in electronic units) ; it determines the decay of cosmic rays passing matter. We give as example the formula of Bethe and Heitler, representing the loss of energy per unit length in a medium containing N nuclei of the atomic number Z per unit volume, for electrons with an energy larger than ϵ, but smaller than $\frac{\epsilon}{\alpha} = 137\,\epsilon$:

$$-\frac{dE}{dx} = N q E,$$

where the effective cross-section in electronic units is

$$q = Z^2 \alpha \left(4 \log 2E - \frac{4}{3} \right)$$

a numerical function depending on $\alpha = \frac{1}{137}$. These examples which could easily be extended show how the number 137 is the dominating factor for all natural phenomena.

8. A Unitary Theory of the Electromagnetic Field.

But this number 137 itself is not explained by the existing theories. This is a very unsatisfactory situation. We are compelled to look for improvements. For this purpose it is necessary to find out the weak points, both deviations of theoretical predictions from experience and internal logical difficulties. As to the first point there is general agreement that there are deviations. Very fast particles are much less absorbed than the theory predicts. This is proved by the enormous penetrating power of the cosmic rays. The retardation of electrons by nuclei with emission of light, mentioned in the last section as the most effective cause of absorption, would stop the cosmic radiation in a metre of water whereas this radiation is still be found at the bottom of deep lakes in some 500 m. deep. In some cases the retardation of single electrons by passing a plate of lead has been measured ; a Wilson cloud chamber combined with a powerful magnet shows curved tracks, and the increase of curvature of a track passing a lead plate allows to calculate the retardation. For particles with an energy larger than 100ϵ the decrease of velocity was found decidedly less than what theory predicts.

Looking for internal logical difficulties we remember the rather shocking way by which the " radius of the electron " was introduced. Unable to bring the assumption of finite dimensions of the electron in accord with Maxwell's field equations the physicists agreed silently to make use of the electronic radius defined by $a_0 = \frac{e^2}{mc^2}$, and to consider at the same time the electron as a point charge !

It is evident that the field equations have to be changed in such a way that the electron gets a finite radius and the " coherence " forces necessary to keep the charge distribution together satisfy the postulate of relativity. Since in the expression for a_0 the constant $\hbar$ does not appear, it seems to be very improbable that this problem has anything to do with quantum theory. Therefore it has been attacked from the standpoint of classical theory on very many different ways. Two main ideas can be distinguished. One way initiated by Einstein introduces gravitation as the internal cause of the coherence of the electron, and endeavours to accomplish this by a unification of the gravitational and the electromagnetic field. Many " unified field theories " have been published, by Einstein, Weyl, Eddington, Veblen and many others, but without success. I believe that this is quite natural. Gravitation is a very weak force, which we know experimentally only from macroscopic, electrically neutral bodies. It seems to me very doubtful whether it has a meaning at all, to talk about the gravitation of two electrons. The gravitational attraction between these electrons in the distance r is

$\kappa \frac{m^2}{r^2}$, where $\kappa = 6{\cdot}664 \times 10^{-8}$ dyne $\frac{cm^2}{g^2}$ is the constant of gravitation, whereas the electric repulsion is $\frac{e^2}{r^2}$. The relation gravitational to electrical force is $\kappa \frac{m^2}{e^2} = 2{\cdot}4 \times 10^{-43}$. The extreme smallness of this factor is a convincing argument that the idea of explaining the elementary particles with help of gravity and all the attempts of unified field theories are entirely wrong.

The other way of a modification of Maxwell's field equations was first tried by Mie in 1912 who showed that these equations allow very great generalisations without losing their shape and invariance properties. He developed an admirable formation of a non-linear field theory, but made unnecessary assumptions which led him to so serious difficulties that this line of research has been nearly forgotten, until I took it up recently.

A direct introduction of a length (the radius of the electron) in any kind of field equations seems impossible if the charges are considered as concentrated in points. For these equations, as given by Mie, have the general form

$$\dot{\vec{D}} = \text{rot}\,\vec{H}, \qquad \text{div}\,\vec{D} = 0,$$

$$\dot{\vec{B}} = -\,\text{rot}\,\vec{E}, \quad \text{div}\,\vec{B} = 0.$$

where the components of the vectors $\vec{D}$, $\vec{H}$ are functions of the components of $\vec{B}$, $\vec{E}$; as the equations are homogeneous in x, y, z, ct, they do not permit any simplification by the introduction of a " natural " unit of length. But since the relation between $\vec{D}$, $\vec{H}$ and $\vec{B}$, $\vec{E}$ is not linear, there is the possibility of introducing a natural unit for the field. The following assumption turned out to be successful :

$$D_x = -\frac{\partial L}{\partial E_x}, \cdots, H_x = \frac{\partial L}{\partial B_x}, \cdots\cdots$$

where

$$L = b^2 \left\{ \sqrt{1 + \frac{1}{b^2}(\vec{B}^2 - \vec{E}^2) - \frac{1}{b^4}(\vec{B} \cdot \vec{E})} - 1 \right\}.$$

This function L is called " Lagrangian ". In the case of Maxwell's equations *in vacuo* it is $L = \frac{1}{2}(\vec{B}^2 - \vec{E}^2)$, whence it follows that $\vec{D} = \vec{E}$, $\vec{H} = \vec{B}$. The new function L is a generalisation thereof ; it contains a constant b called the " absolute field ", which is supposed to be very large. If $\vec{B}$, $\vec{E}$ are small compared with b, L reduces in first approximation to Maxwell's

expression $L_r = \frac{1}{2}(\vec{B}^2 - \vec{E}^2)$. Infeld and I have shown that L_r is the simplest function fulfilling all conditions of relativity.

As Mie has already shown, the laws of conservation of electromagnetic energy and momentum can be derived from the field equations, in the form of divergence-equations. For instance the law of conservation of energy is

$$\frac{\partial U}{\partial t} + \operatorname{div} \vec{S} = 0$$

where

$$U = L_r + \vec{E}\,\vec{D}, \qquad \vec{S} = \vec{E} \times \vec{H}$$

are the densities of energy and momentum. There is a static solution ($\vec{H} = 0$, $\vec{B} = 0$) corresponding to a point charge. For the equation $\operatorname{div} \vec{D} = 0$ has the centre-symmetric solution $D_r = \frac{e}{r^2}$, and one has

$$D_r = -\frac{\partial L_r}{\partial E_r} = \frac{E_r}{\sqrt{1 - \frac{1}{b^2} E_r^2}},$$

or

$$E_r = \frac{D_r}{\sqrt{1 + \frac{1}{b^2} D_r^2}} = \frac{e}{\sqrt{r_0^4 + r^4}},$$

if r_0 is defined by

$$b = \frac{e}{r_0^2}.$$

E_r is everywhere finite; for large r, compared with r_0, one has $E_r \to \frac{e}{r^2}$, *i.e.*, Coulomb's law, but for small r E_r does not become infinite, but assumes for $r = 0$ the value $\frac{e}{r_0^2} = b$. The absolute field constant is therefore the field in the centre of the electron. Since this theory is relativistically invariant, Einstein's law $E = mc^2$ is exactly fulfilled. A simple calculation gives for the rest-energy

$$E = mc^2 = \int U \, dx \, dy \, dz = 1{\cdot}236 \frac{e^2}{r_0}.$$

This formula can be considered as exact definition of the "radius of the electron", which deviates from the "conventional" radius a_0 by a numerical factor:

$$r_0 = 1{\cdot}236 \frac{e^2}{mc^2} = 1236 \, a_0.$$

Here we have the principal point: The new theory considers matter and field not as two entities, but as one and the same. The particles are

simple singularities of the field, and their mass is the field energy connected with the singularities. It is a *unitary field theory*, in opposition to the accepted dualistic theories which introduce separate masses for each kind of particles.

We cannot enter into a discussion of other consequences of this theory, but we shall restrict ourselves to the question connected with the mystical number 137. There is little hope that this new theory of the electromagnetic field can help us immediately to understand this number; for as it was defined with the help of $\hbar$ it must be connected with quantum ideas and can never be derived from a purely classical theory. The new field theory removes the difficulties connected with the "radius of the electron" (or with the infinite self-energy of the electron as a point charge), but it is certainly only a limiting case of a quantum electro-dynamics, just as classical mechanics is a limiting case of quantum mechanics (Bohr's correspondence principle).

9. *Quantum Electrodynamics.*

The idea of light quanta or photons, as proposed by Einstein for the explanation of the photoelectric effect, was the first indication that quantum principles had to be applied to the electromagnetic field in the empty space.

For this purpose one considers the field as composed of harmonic waves, by a Fourier analysis; then each Fourier-coefficient, representing the amplitude of a monochromatic wave, can be treated as mechanical coordinate and subject to quantum conditions. In this way it was possible to give an exact meaning to the notion of a photon and to derive the laws of statistical equilibria of those, *i.e.*, Planck's law of radiation and the fluctuation of radiant energy. Dirac succeeded in giving a rigorous treatment of emission, absorption and scattering of light by considering an atom and its surrounding field as a quantised system.

Later Pauli and Heisenberg gave the theory a form which did not make use of the Fourier decomposition of the field components, but treated these directly as quantum variables. This method can be transferred to the unitary field theory, in the following way:

The components of the vectors $\vec{D}$ and $\vec{B}$ have to be taken as primary variables; just as in quantum mechanics q and $p = \frac{\hbar}{i}\frac{\partial}{\partial q}$ do not commute $\left\{\text{one has } (pq - qp)\, f(q) = \frac{\hbar}{i}\left[\frac{\partial}{\partial q}(qf) - q\frac{\partial f}{\partial q}\right] = \frac{\hbar}{i} f, \text{ or } pq - qp = \frac{\hbar}{i}\right\}$ some components of $\vec{D}$ and $\vec{B}$ are supposed not to commute. $\vec{D}, \vec{B}$ are functions of the space vector $\vec{r}$ (x, y, z) and time t; x, y, z, t are considered as commuting variables. The assumption is made that any components of $\vec{D}$ and $\vec{B}$

commute, when they are taken in two points at finite distance, but that this fails to hold, if the two points approach. One has commutation laws as:

$$D_y\left(\vec{r}_1, t\right) \cdot B_z\left(\vec{r}_2, t\right) - B_z\left(\vec{r}_2, t\right) \cdot D_y\left(\vec{r}_1, t\right) = \hbar c \frac{\partial}{\partial x} \delta\left(\vec{r}_1 - \vec{r}_2\right).$$

$\delta\left(\vec{r}_1 - \vec{r}_2\right) = \delta(x_1 - x_2) \cdot \delta(y_1 - y_2) \cdot \delta(z_1 - z_2)$ is the product of three symbolic δ-functions of Dirac. $\{\delta(x)$ is 0 for $x \neq 0$, but ∞ for $x = 0$ in such a way that $\int_{-\infty}^{\infty} \delta(x)dx = 0\}$.

If $\vec{D}$, $\vec{B}$ are expressed as multiples of the absolute field constant b, one gets

$$D_y^{(1)} B_z^{(2)} - B_z^{(2)} D_y^{(1)} = \frac{\hbar c}{b^2} \frac{\partial}{\partial x} \delta\left(\vec{r}_1 - \vec{r}_2\right).$$

Since $b = \frac{e}{r_0^2}$, the constant is

$$\frac{\hbar c}{b^2} = \frac{\hbar c}{e^2} r_0^4 = \frac{1}{a} r_0^4.$$

The appearance of the factor r^4 is explained by the fact that the δ-function is not dimensionless, but is of the order $\frac{1}{r^3}$, as its integral over space is unity; therefore $r_0^4 \frac{\partial}{\partial x} \delta$ is dimensionless.

These commutation laws are combined with differential equations giving the change of an operator F in space and time:

$$\frac{\hbar}{i} \frac{\partial F}{\partial t} = WF - FW$$

$$\frac{\hbar}{i} \frac{\partial F}{\partial x} = -(p_x F - F p_x)$$

where

$$W = \int U dv, \qquad \vec{p} = \int \vec{S}\, dv$$

are the total electromagnetic energy and momentum. The energy density U can be taken as any invariant function of $\vec{D}$, $\vec{B}$; in the case of the Lagrangian L given in the last section one has (with $b = 1$):

$$U = \sqrt{1 + \vec{D}^2 + \vec{B}^2 + \vec{S}^2} - 1, \qquad \vec{S} = \vec{D} \times \vec{B}.$$

Then it can be shown that the generalised field equations are a consequence of this assumption.

It can also be shown that a closed system as a whole satisfies the laws of quantum mechanics. Especially its total angular momentum

$$\vec{M} = \int (\vec{r} \times \vec{S})\, dv$$

is quantised, and always an integer multiple of $\hbar$.

This result shows that the theory in this form is incomplete. For we know that electrons (and protons) have the angular momentum $\frac{1}{2}\hbar$. The spin effect is not represented by these equations.

Therefore my collaborator M. H. L. Pryce has proposed a modification of the theory in which the coordinate $\vec{q}$ and the momentum $\vec{\xi}$ of the point charge are introduced as new quantum variables. They are connected with the field by the quantum conditions

$$[D_x, \xi_x] = e\,\delta(\vec{r} - \vec{q}), \cdots$$

The expressions for energy and momentum are modified so as to represent the spin effects; for one singularity they are

$$W = \int U dv + \vec{\alpha} \cdot \vec{\xi},$$
$$\vec{p} = \int \vec{S}\, dv + \vec{\xi}.$$

Here $\vec{\alpha}$ is a vector the components of which are Dirac-matrices α_1, α_2, α_3. Then it can be shown that the field equations follow in the form:

$$\dot{\vec{D}} - \text{rot}\,\vec{H} = 4\pi e\,\vec{\alpha}\,\delta(\vec{r} - \vec{q}), \quad \text{div}\,\vec{D} = 4\pi e\,\delta(\vec{r} - \vec{q}),$$
$$\dot{\vec{B}} + \text{rot}\,\vec{E} = 0 \qquad\qquad \text{div}\,\vec{B} = 0.$$

They have now δ-functions on the right hand term, corresponding to a point charge at the point $\vec{q}$ moving with the velocity $\vec{\alpha}$.

The total angular momentum of a closed system is now the vector sum of the electromagnetic momentum $\int(\vec{r} \times \vec{S})\, dv$ and the spin momentum $\frac{1}{2}\hbar$. This formalism seems to give the possibility of adapting Dirac's spin theory to the general idea of the non-linear field equations in which the particles appear as singularities.

But on the other hand the equations of Pryce do not agree well with our aim to explain the number 137. For as the commutation rules of the field components contain the constant $\hbar$, the ideal theory should not introduce e as an independent constant as is the case in Pryce's commutation rule for $\vec{D}$ and $\vec{\xi}$.

Nevertheless this theory can be adopted as a step in the right direction, as the following considerations show.

10. The Mass of the Proton.

As we have seen, the total angular momentum of a closed system is the vector sum of the real electromagnetic momentum $l\hbar$, with $l = 0, 1, 2, \cdots$,

and the spin momentum of the singularities, $\frac{1}{2}\hbar$. The quantum number of the total momentum j has therefore the values $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \ldots\ldots$, but to each value of j correspond two states : $l + \frac{1}{2}$ and $(l + 1) - \frac{1}{2}$. All this is well known from the theory of the spectra, where the azimutal quantum number l of the orbital motion combines with the spin $\frac{1}{2}$ to the so-called inner quantum number j. But whereas the two states with the same j have nearly the same energy in the case of the spectra so that the spin leads only to a fine structure of the lines the application of this idea to the point charge, as singularity of the non-linear field equations, leads to a very gross structure indeed : it gives the enormous difference of the internal energies of the proton and the electron.

This idea has been suggested by Pryce. He started from the experimental fact that both kinds of particles, protons and electrons have the same angular momentum. As the spin is not connected with an accumulation of energy, the state $0 + \frac{1}{2}$ with no electromagnetic momentum ($l = 0$) should have only electrostatic energy, whereas the state $1 - \frac{1}{2}$ which has a finite electromagnetic momentum ($l = 1$), has an additional electromagnetic energy, which might explain the great mass difference.

I shall show that this conjecture is strongly confirmed by an estimate of the energies. A correct calculation would of course imply the exact solution of the problem of our field equations, not only as classical differential equations, but as a quantum problem. We are far from being able to solve this problem. But for an estimate of the order of magnitude this is not necessary. It suffices to combine some well-established knowledge.

We know from experiments of Stern the magnetic moment of the proton. It is of the order of magnitude which one expects if the electronic mass m in the expression for the magneton $\mu = \frac{\hbar e}{2mc}$ is replaced by the mass of the proton M ; yet it is not exactly equal to the "nuclear magneton" $\frac{M}{m}\mu = 1840\,\mu$, but about $2\frac{1}{2}$ times larger. This shows that the magnetic moment of the proton is not a primary effect like that of the electron, but may be the result of two nearly compensating actions. This fits very well with Pryce's idea of the proton being the state $1 - \frac{1}{2}$ of the elementary charge. We know that the magnetic moments of the spin and of the orbital motion of the electron in an atom running around a nucleus, are equal, both one Bohr magneton, in spite of the difference of the mechanical momentum. It is natural to assume that the same holds for the magnetic moment of the electromagnetic field of the elementary charge itself. The two motions characterised by $l = 1$ and $s = \frac{1}{2}$ would compensate their magnetic moments,

if there would be no interaction between them. This interaction may be responsible for the small difference, about $2\frac{1}{2}$ nuclear magnetons; but this question does not interest us.

We try now to estimate the energy of the rotating electromagnetic field with the magnetic moment μ. As an exact calculation is impossible we use the analogy of the electrostatic case. There we know that the unitary field theory gives an expression of the same form $A\frac{e^2}{a_0}$ for the energy of a point charge, as the classical theory for a charged sphere, only with a little different numerical coefficient A. We can safely suppose that the same holds in the magnetic case. Now the magnetic energy of a magnetised sphere of the radius a_0 with the moment μ is $\frac{1}{2}\frac{\mu^2}{a_0^3}$. We can be confident that this holds also in the unitary theory with respect to order of magnitude. Here we introduce the value $\mu = \frac{ea_0}{2\alpha}$. As we shall see immediately the resulting expression for the magnetic energy is large compared with the electrostatic energy, and we can identify it with the total energy Mc^2 of the rotating charge. So we find

$$Mc^2 = \tfrac{1}{2}\frac{e^2a_0^2}{(2\alpha)^2}\frac{1}{a_0^3} = \frac{1}{8\alpha}\frac{e^2}{a_0}.$$

On the other hand the electrostatic energy of the point charge is

$$mc^2 = \frac{e^2}{a_0}.$$

From this follows

$$\frac{M}{m} = \frac{1}{8\alpha^2} = \frac{(137)^2}{8} = \frac{18770}{8} = 2340.$$

This agrees fairly well with the mass quotient 1840 of proton and electron, for the numerical coefficients are rather arbitrary. But the appearance of the factor $\frac{1}{\alpha^2}$ is quite unambiguous, and it is responsible for the order of magnitude.

If the idea is correct, that the positron and the proton, the electron and the (hypothetical) negative proton are different states of the same elementary charge, one should expect to find transitions; for instance from a proton to a positron under emission of light quanta. The energy of these should be of the order Mc^2 or 1840 mc^2, and since mc^2 corresponds to about $\frac{1}{2}$ million electron volts, this radiation would have an energy of about 1000 million volts.

Now the objection can be raised: why do then exist protons at all? And when a proton is generated from a positron by absorption of energy, why does it not spontaneously jump back in its initial state?

The answer is given by the consideration that a rotating charge distribution of one sign has no electric moment; it cannot emit a dipole radiation, but only a quadrapole radiation (of the magnetic type). But it is well-known that in this case the rotational quantum number changes by 2, not by 1. Hence the state $l = 1$ is metastable, it cannot go over into the state $l = 0$ by emission of radiation.

But collisions with fast electrons may induce such a transition. Therefore one might expect the occurrence of transformations of protons into positrons in matter bombarded by cosmic rays. Such process would involve most violent emission of light quanta from one point of the space, like an enormous explosion, which may accelerate the surrounding electrons of the atom, or may produce a number of electronic pairs (an effect, of which we have to speak in the next section).

Explosions of such kind have been observed by Hoffmann as "Stösse," or bursts, in an ionisation chamber; it is not settled whether the "showers of" particles (positive and negative electrons) discovered by Blackett and Occhialini are small bursts, or something different. No satisfactory explanation of bursts and showers has been given on the accepted theories. I should like to propose the idea that we have in the bursts the affects of the transformation of protons into positrons.

The hypothesis of the intrinsic identity of the light and heavy particles, being different rotational states of the same singularity of the electromagnetic field reduces one of the mysterious numbers, 1840, to the other, 137. But the problem of the latter is not solved, not even approached. It seems extremely difficult to understand the formula for the magneton $\mu = \frac{ea_0}{2a} = 68 \cdot 5ea_0$, because of the big numerical factor. Classical considerations are very unlikely to be of any use. The general formula for the magnetic moment of rotating charges is $\mu = \frac{1}{2c} \Sigma e (\vec{r} \times \vec{v})$. If one takes for v the maximum value c and concentrates all charges in one distance R, one has $\mu = \frac{1}{2} eR$; therefore the efficient radius should be $\frac{a_0}{a} = 137a_0 = \frac{\lambda_0}{2\pi}$ where λ_0 is the Compton wave-length. This consideration reveals the root of the difficulty: the existence of two different natural units of length, the electrostatic unit a_0 and the quantum unit $\frac{\lambda_0}{2\pi}$, in the relation a.

11. Attempts to explain the Mysterious Number.

We have given the value of $\frac{1}{\alpha}$ as a whole number 137. The reason is simple, *viz.*, that the accuracy of measurement does not seem to suffice for a determination of the next figure. There are two ways, either measurements of e, $\hbar$ and c, from which $\alpha = \frac{e^2}{\hbar c}$ can be computed; or direct measurements of the fine structure of hydrogen like atoms. The latter method has been improved recently by using heavy hydrogen, or deuterium D; by comparing the fine structure of H and D one can reduce the determination of α to a relative measurement. The result seems to be that $\frac{1}{\alpha}$ is decidedly greater than 137, about 137·2. I believe that we have no reason to assume that $\frac{1}{\alpha}$ is a whole number.

But some years ago, when the numerical value was still less known, Eddington proposed a theory in which $\frac{1}{\alpha}$ should be a whole number 136. This figure was supposed to be the expression $\frac{1}{2} n^2 (n^2 + 1)$ for $n = 4$, representing something like the "number of freedom" of the Dirac electron (which is described by matrices with 4 lines and columns). Later, when it became clear, that $\frac{1}{\alpha}$ was more likely to be 137 than 136 he changed his theory so as to add a unit. He also developed a formula for the mass quotient which was found to be the root of quadratic equations in which besides 136 the number 10 played a rôle, 10 being the value of $\frac{1}{2} n^2 (n^2 + 1)$ for $n = 2$.

I was never able to understand this theory which seems to be itself rather mystical.

We shall turn now to the question how to explain the number 137 from the standpoint of the theories discussed here.

As $\alpha = \frac{e^2}{\hbar c}$ connects the constants e and $\hbar$ one must either assume the existence of smallest electric charges e and reduce the quantum constant $\hbar$ to it, or *vice versa*.

Now we know that charges can be born or disappear. This fact which was first foreseen by Dirac's theory of the positron and is evident from the standpoint of the unitary field theory has been stated experimentally without doubt. Light quanta passing the field of a nucleus can produce a pair of electrons, one positive, the other negative; and such a pair can vanish by neutralisation, emitting light quanta.

The laws of this materialisation effect can be derived from Dirac's quantum mechanical theory, as we shall see immediately. Therefore it seems natural to assume $\hbar$ as primary quantity and to try an explanation of the birth of electrical quanta. Let us consider this first from the standpoint of the unitary field theory as classical differential equations. Here the electron and the positron are represented by two equal and opposite point charges surrounded by a static field. If the distance of the singularities is large compared with a_0 one can consider the field separately for each charge. But when the electrons approach, the fields melt together, as the equations are not additive. This process can be followed in all details in a special case, namely for two dimensions and infinitely slow motions. My collaborator Pryce has developed the exact solution for this case. The formulæ describe how the field concentrates and disappears when the charges approach till they coincide. But this quasi-static process would need forces keeping the charges in their instantaneous positions. If they are left free, they will be accelerated towards another, generating a magnetic field. As this has the tendency to persevere (electromagnetic inertia), the pair of charges will shoot over the position of neutralisation and appear with reversed signs. It constitutes a kind of oscillator or dipole the binding force of which is determined by the field itself. The oscillations will be damped as energy is sent out in form of spherical waves. In this way the amplitudes diminish till the neutralisation is perfect and all the energy is radiated away.

The disappearance of a pair is therefore connected with a vibration " around the nothing". The frequency of this vibration must be determined by the constants of the field theory c, b and e. The only quantity of the dimension of reciprocal time which can be built out of these is $c\sqrt{\frac{b}{e}} = \frac{c}{r_0}$; the frequency of neutralisation must therefore be of the form $\nu = \gamma \frac{c}{r_0}$, where γ is a numerical constant.

If there is any correspondence between this classical consideration and the real quantum process of neutralisation, this ν should be the Compton frequence, $\nu_0 = \frac{c}{\lambda_0} = \frac{mc^2}{h}$. For having conservation of momentum, the light emitted must consist at least out of 2 photons; the energy $2mc^2$ disappears, therefore one has $mc^2 = h\nu_0$.

Introducing here $mc^2 = 1 \cdot 236 \frac{e^2}{r_0}$ and $v_0 = \gamma \frac{c}{r_0}$ one gets

$$\alpha = \frac{e^2}{\hbar c} = \frac{2\pi\gamma}{1 \cdot 236}.$$

Here we have a new interpretation of α: it is determined by the neutralisation frequency of an electron pair.

The only existing real attempt to calculate α has an intimate connection to this idea.

As we said, Dirac has explained the existence of positive electrons and the neutralisation of pairs from the standpoint of his wave equation. This equation has a property which was considered first as a great disadvantage: it gives states of negative energy. The energy of a free electron is given by the relativistic expression $E = c\sqrt{m^2c^2 + p^2}$, where p is the momentum; here the square root can have both signs. The possible values of E are therefore the positive numbers $\geqslant mc^2$ and the negative numbers $\leqslant -mc^2$. To overcome this difficulty Dirac assumed that all states of negative energy are generally filled up by (negative) electrons, using Pauli's principle that no state can contain more than one electron (confirmed by the laws of atomic spectra). Only occasionally, for instance by the action of a photon, an electron can be thrown out of a state of negative energy. Then it appears as a normal electron, but at the same time there remains a "hole" in the lake of electrons with negative energy, and this hole behaves exactly like a positive electron with positive energy. If the electron falls down into the hole under emission of photons, the pair vanishes.

This strange idea has proved itself to be very fruitful as it leads to formulæ for the yield of birth or death of pairs in fair agreement with experience. These effects can apparently be treated as simple acts of emission or absorption, only that one of the states concerned has a negative energy value. The theory allows us to calculate the effective cross-section for the generation of a pair by a photon $h\nu$ in the field of nucleus of charge Ze:

$$q = \frac{1}{2\pi} r_0^2 Z^2\alpha^2 \frac{28}{9}\left(\log\frac{2h\nu}{mc^2} - \frac{218}{27}\right),$$

and this formula represents the facts with astonishing accuracy.

But on the other hand this theory leads to immense intrinsic difficulties. It is compelled to assume that the infinity of electrons with negative energy do not generate a field, but are attacked by fields (otherwise light would not make pairs). The distinction between positive and negative energy values is clear only in the case of free electrons; if fields are present, it breaks down. Further the difficulty of the "infinite self-energy" of the electron which is the trouble of each theory using Maxwell's equations appears here enlarged by other infinities, arising from the infinite number of electrons in the states of negative energy.

Dirac and Heisenberg have tried to overcome these difficulties by subtracting the electric density of the negative states from the actual density. But as both are infinite numbers their difference is not uniquely determined and there is a great deal of arbitrariness in these assumptions.

Nevertheless, there are definite equations stated by these authors which claim to represent the motions of positive and negative electrons, and these equations have one property in common with the unitary field theory: they are not linear. These non-linear terms give rise to an effect which can also be derived from the unitary field theory (but not from Maxwell's equations): scattering of light by light. It can be interpreted from the standpoint of Dirac's theory in the following way: Two incident photons can be instantaneously absorbed giving rise to a pair of electrons; but these collapse immediately under emission of two other photons. The total effect looks like a collision of the photons. But it is intimately connected with the generation and neutralisation of a pair. This is the connection with the classical consideration given above. But whereas the permanent production of a pair cannot be calculated from the standpoint of the unitary field theory, this scattering effect can be treated easily and the comparison of the results of both methods gives the connection between e and $\hbar$ which we are looking for.

This method has been worked out by two pupils of Heisenberg, Euler and Kockel. They calculate the scattering of light by light from the Dirac-Heisenberg theory of " holes " and show that it can be expressed as a result of non-linear correction terms to Maxwell's equation, corresponding to a Lagrangian

$$L = \tfrac{1}{2}(\vec{B}^2 - \vec{E}^2) - \frac{1}{90\pi}\left(\frac{e^2}{m^2c^4}\right)^2 \frac{1}{a}\left\{(\vec{B}^2 - \vec{E}^2)^2 + 7\,(\vec{B}\cdot\vec{E})^2\right\}.$$

This can be compared with the Lagrangian of the unitary field theory developed into a power series:

$$L = b\left\{\sqrt{1 + \frac{1}{b^2}(\vec{B}^2 - \vec{E}^2) - \frac{1}{b^4}(\vec{B}\cdot\vec{E})^2} - 1\right\}$$

$$= \tfrac{1}{2}(\vec{B}^2 - \vec{E}^2) - \frac{1}{8b^2}\left\{(\vec{B}^2 - \vec{E}^2)^2 + 4\,(\vec{B}\cdot\vec{E})^2\right\} + \cdots.$$

There is no full coincidence of the second order term, as the coefficients of the term $(\vec{B}\,.\,\vec{E})^2$ differ from another.

Neglecting this point, we can equate the coefficients:

$$\frac{1}{90\pi}\left(\frac{e^2}{m^2c^4}\right)^2 \frac{1}{a} = \frac{1}{8b^2}.$$

Now we have

$$b = \frac{e}{r_0^2}, \quad mc^2 = 1 \cdot 236 \, \frac{e^2}{r_0},$$

and it follows

$$\frac{1}{a} = \frac{45\pi(1 \cdot 236)^4}{4} = 82 \cdot 4.$$

This is smaller than the experimental value 137 by the factor 1·66, but it is of the right order of magnitude. Considering the arbitrary assumptions made in the Dirac-Heisenberg theory the discrepancy seems not to be discouraging. In any case, it gives the first order terms of the unitary field theory. But the numerical factor 1·236 in the connection between mc^2 and $\frac{e^2}{r_0}$ rests on a classical calculation which is really an unjustified extrapolation into the interior of the electron.

An observation of the scattering of light by light is not possible owing to the smallness of the effect. The cross-section is of the order

$$q = r_0^2 \, \frac{1}{a^4} \left(\frac{r_0}{\lambda}\right)^6$$

equal to about 10^{-30} cm.^{2} for γ-rays, 10^{-70} cm.^{2} for visible light.

12. Conclusion.

Proposing the idea of a unitary field theory I am aware of being in opposition to the most eminent physicists, as Bohr, Pauli, Heisenberg. They seem to have the idea that a perfect theory should express the laws of the motion of the elementary particles by wave equations, each particle having a given charge and mass; the electromagnetic field shall play only the rôle of a fiction invented to represent the finite velocity of the propagation of the interaction of the particles in a convenient way. My objection to this programme is that I cannot see how it ever could explain the existence of the heavy and light elementary particles and their definite mass quotient 1840, and the relation of the charge to the quantum constant expressed by the number 137.

But it may turn out that both ways lead to the same result, as the consideration of the last section shows an intimate relationship between them. Just as quantum mechanics can be considered as a reconciliation of the ideas of particle and wave by a critical review of the fundamental motions of space-time and energy-momentum, the physics of the future may be an amalgamation of the ideas of quantum and charge with help of a critical study of the notions used for the description of the electromagnetic field and its singularities.

VINOGRADOW'S SOLUTION OF WARING'S PROBLEM: HYPOTHESIS K OF HARDY AND LITTLEWOOD.

By Inder Chowla.

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Introduction.

Let $G(n)$ denote the least s such that every large number is a sum of s nth powers $\geqslant 0$. Vinogradow[1] has recently proved that

$$G(n) = O(n \log n).$$

On the basis of an unproved result, namely:

Hypothesis K. *The number of representations of* N *as a sum of* n n*th powers* $\geqslant 0$ *is* $O(N^{\epsilon})$ *for any* $\epsilon > 0$, Hardy and Littlewood[2] proved that

$$G(n) \leqslant \text{Max } [2n + 1, \Gamma(n)]$$

where $\Gamma(n)$ may be defined as the least s such that every arithmetical progression contains an infinity of numbers of the form $x_1^n + x_2^n + \cdots + x_s^n$ where the x's are required to be integers.

We shall denote by $H_{n,n}(x)$ the number of positive integers not exceeding x which are expressible as a sum of n nth powers $\geqslant 0$. We note that the hypothesis that

Hypothesis P. $H_{n,n}(x) > x^{1-\epsilon}[x > x_0(\epsilon)]$ *for any positive* ϵ is less drastic than Hypothesis K.

Pillai has recently modified Vinogradow's method so as to prove the following results :—

I. *If Hypothesis* P *is true then*

$$G(n) \leqslant \text{Max } [n+1, \Gamma(n)] + 2n + 1.$$

II. *Every large number is a sum of* $\Gamma_1(n)+1$ nth *powers* $\geqslant 0$ *and* 2 *primes, where* $\Gamma_1(n) = \text{Max } [n+1, \Gamma(n)]$.

In this paper we use the methods of Hardy, Littlewood and Vinogradow, coupled with ideas from Pillai, to prove the following result.

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[1] *Annals of Mathematics*, 1935, **36**, 395–405.

[2] *Math. Ztschr.*, 1925, **23**, 1–37. (We shall refer to this paper as P.N. VI.)

III. *There exists a number* w, *depending only on* n, *with the following property. If Hypothesis* P *is true then every large number* $\equiv 1 \pmod{w}$ *is expressible as a sum of* $(3n+2)$ *nth powers* $\geqslant 0$. *Here* $n > n_0$. This result is deduced from

IV. *If* n *is greater than* n_0, *and*

$$H_{n,n}(x) > > x^{1-\frac{1}{n(n-1)2^{n+2}}}$$

then there exists a 'w' *depending only on* n *such that every large number* $\equiv 1 \pmod{w}$ *is a sum of* $(3n+2)$ *nth powers* $\geqslant 0$.

Some special cases of III are worthy of mention. Let us write

$$(m)^k = (n)^k$$

when there exist non-negative integers x_s $(s \leqslant m)$, y_t $(t \leqslant n)$ such that

$$\sum_{s=1}^{m} x_s^k = \sum_{t=1}^{n} y_t^k$$

and

x_s $(s \leqslant m) \neq y_t$ $(t \leqslant n)$ and further where at least one x or y is different from zero; also $(x_1, \cdots, x_m, y_1, \cdots, y_n) = 1$. It is not yet known whether (and this is a problem of great interest)

$$(k)^k = (k)^k$$

is always possible (proved for[3] $k \leqslant 10$). Another problem of exceptional interest is that of determining the least m for which

$$(1)^k = (m)^k$$

is possible. If Fermat's last theorem is true then $m \geqslant 3$. All existing computational evidence seems to indicate that $m \geqslant k$. It is a consequence of our results that

V. *For* $k > k_0$ *at least one of the following two relations is true:*

(i) $(k)^k = (k)^k$

(ii) $(1)^k = (3k+2)^k$.

Lemma 10 of this paper, essential to the success of the argument, is due to S. Chowla. My thanks are due to him for guidance and help in the preparation of this paper.

In the body of the paper we introduce certain conditions A, B, $\cdots$, G_1, G_2, $\cdots$, N. At the end of the paper we show that these conditions are actually satisfied.

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[3] See, for example, Rao, "On Sums of Sixth Powers", *Jour. London Math. Soc.*, 1934, **9**, 172; Inder Chowla, "Note on Sums of Sixth Powers", *ibid.*, 1935, **10**, 233; Maitland Wright, "On Sums of kth Powers", *ibid.*, 1935, **10**, 94–99; S. Chowla and S. Sastry, "On Sums of Powers", *Proc. Indian Acad. Sci.*, (A), 1935, **1**, 534–535.

§1. *Notation and Lemmas.*

$$B_{a,q} = \frac{1}{q} \sum_{r=0}^{q-1} \exp\left(2\pi i \frac{a}{q} r^n\right) \text{ where } (a,q) = 1;$$

$$A(q) = A(N, n, t, q) = \sum_{\substack{1 \leqslant a \leqslant q \\ (a,q)=1}} B_{a,q}{}^t \, e^{-2\pi i \frac{a}{q} N}$$

$$S(N) = S(N, n, t) = \sum_{q=1}^{\infty} A(N, n, t, q);$$

$$S(N) = \prod_p \chi_p$$

where

$$\chi_p = 1 + A(p) + A(p^2) + \cdots;$$

$M(p^l, N, t,) = M(p^l, N)$, the number of solutions of $\sum_{\nu=1}^{t} h_\nu{}^n \equiv N (p^l)$

for $0 \leqslant h_\nu < p^l \quad (l \geqslant 0)$; p_r is the rth prime;

$$\gamma = \gamma_r = \begin{cases} \theta_r + 1 & \text{for } p = p_r > 2, \\ \theta_r + 2 & \text{for } p = p_r = 2, \end{cases}$$

where $p_r{}^{\theta_r}$ is the highest power of p $(= p_r)$ contained in n; (λ) denotes the distance of λ from the nearest integer; $v = \frac{1}{n}$; $d(m)$ is the number of divisors of m.

$$P = [\tfrac{1}{3} N_0{}^v + 1]; \; P_1 = [n^v P^{1-v}]; \; R = [P^a]; \; \tau = [2n 3^{n-1} P^l];$$

$$T = \sum_{x=1}^{P} e^{2\pi i \alpha x^n}, \; T_1 = \sum_{x=1}^{3P} e^{2\pi i \alpha x^n};$$

$S = \sum_{\xi} e^{2\pi i \alpha \xi}$ where the sequence of numbers ξ will be defined later;

$V = \sum_{v} e^{2\pi i \alpha v^n}$ where v runs through the values $P, P+1, \cdots, 2P-1$;

$V_w = \sum_{v_1} e^{2\pi i \alpha w^n v_1{}^n}$ where v_1 runs through the values $R, R+1, \cdots, 2R-1$;

$N_0 - N_0 p^{-\theta} < N \leqslant N_0$; $c, c_0, c_1, \cdots$ positive numbers depending only on n;

$A << B$, $B >> A$, $A = O(B)$, where B is positive, signify that $|A| \leqslant c_0 B$.

The numbers ξ are less than or equal to $P_1{}^n$, and the number X of numbers ξ between 1 and $P_1{}^n$ (both limits inclusive) has the property that $X >> P^{n-1-\sigma}$. There is no danger of confusing this σ with that of Lemma 6.

We define the numbers u by

$$u = \xi + v^n.$$

It is evident that the numbers u are all different and possess the property $P^n \leqslant u < (2P)^n$. $H_{n,s}(x)$ denotes the number of positive integers not exceeding x which are expressible as a sum of s nth powers $\geqslant 0$. We note that the hypothesis

$$(A) \quad H_{n,n}(x) >> x^{1-\rho}$$

is less drastic than

$$(B) \quad r_{n,n}(x) << x^{\rho}.$$

since (A) is certainly true if (B) is true but the converse does not hold.

Lemma[4] 1.

$$B_{a,q} << q^{-\nu}.$$

Lemma 2.

$$\sum_{q>\nu} |A(q)| << \nu^{-c} \{d(N)\}^3 \quad (t \geqslant n+1).$$

Lemma 3.

Let

$$0 \leqslant f'(t) \leqslant \tfrac{1}{2}, \quad f''(t) \geqslant 0,$$

in the interval $g \leqslant t \leqslant h$. *Then*

$$\sum_{t>g}^{h} e^{\pm 2\pi i f(t)} = \int_g^h e^{\pm 2\pi i f(t)}\, dt + O(1).$$

Lemma 4.

If λ *be a real but not an integral number and* $G < H$, *then*

$$\left| \sum_{x>G}^{H} e^{2\pi i \lambda x} \right| < \frac{1}{2(\lambda)}.$$

Lemma 5. *For* $l \geqslant 0$

$$\sum_{\lambda=0}^{l} A(p^{\lambda}) = p^{-(l-1)l} M(p^l).$$

Lemma 6. *Let the highest power of* p *in* N *be* $\beta n + \sigma$ $(\beta \geqslant 0, 0 \leqslant \sigma < n)$. *Let* $l_0 = \mathrm{Max}\,(\beta n + \sigma + 1, \beta n + \gamma)$.

Then $A(p^l) = 0$ *for* $l > l_0$.

Lemma 7. *For* $t \geqslant 5$, $p > b = b(n, t)$, $\chi_p > 1 - p^{-\frac{5}{4}}$

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[4] Lemmas 1, 3, 4 are from Vinogradow's paper; lemma 2 is lemma 5 of P.N. VI; lemmas 5, 6, 7, 8 are from Landau's *Vorlesungen uber Zahlentheorie*, Bd. 1, see pages 281, 284, 286 and 255 respectively.

Lemma 8. *If* $(a, q) = 1$, $m > 0$, r *an integer,*

$$S = \sum_{h=r+1}^{r+m} \exp\left(2\pi i \frac{a}{q} h^n\right)$$

then for any arbitrary positive ϵ,

$$|S|^k << m^{\epsilon} q^{\epsilon} \left(m^{k-1} + \frac{m^k}{q} + m^{k-n} q\right) \quad (k = 2^{n-1})$$

By lemma 7 there exists a number b, depending only on n and t, such that

$$\chi_p > 1 - p^{-\frac{5}{4}} \quad (p > b, t \geqslant 5).$$

Let $p_1, \cdots, p_r$ be the primes $\leqslant b$. If $(N, p_s) = 1$ for $1 \leqslant s \leqslant r$ it follows from lemma 6 that

$$A(p_m{}^l) = 0 \text{ for } l > \begin{cases} 1 + \theta_m & \text{for } 2 \leqslant m \leqslant r. \\ 2 + \theta_m & \text{for } m = 1 \end{cases}$$

where $p_m{}^{\theta_m}$ is the highest power of p_m contained in n.
Hence from lemmas 6 and 5

$$\chi_2 = \sum_{\lambda=0}^{2+\theta_2} A(2\lambda) = 2^{-(t-1)(2+\theta_2)} M(2^{\theta_2+2}, N),$$

$$\chi_{p_m} (2 \leqslant m \leqslant r) = \sum_{\lambda=0}^{1+\theta_m} A(p_m \lambda) = 2^{-(t-1)(1+\theta_m)} M(p_m{}^{1+\theta_m}, N).$$

It follows that if $N \equiv 1(Y)$ where $Y = Y(t, n)$

$$= 2^{\theta_2+2} \prod_{2 \leqslant m \leqslant r} (p_m{}^{1+\theta_m}) \text{ then } \chi_{p_m} > 0 \text{ for } 1 \leqslant m \leqslant r.$$

Thus we obtain

Lemma 9. *For every* $t \geqslant 5$ *there exists a number* $Y = Y(t, n)$ *such that for all* $N \equiv 1(Y)$ *the singular series*

$$S(N, n, t) > c$$

where c *is a positive constant depending only on* n *and* t.

In particular with $t = n+1$ we get

Lemma 10. *There exists a number* w, *depending only on* n, *such that for all* $N \equiv 1$ (w), *the singular series*

$$S(N, n, n+1) > c$$

where c *is a positive constant depending only on* n.

The number w occurring in the definition of $V_w = \sum_{v_1} \exp(2\pi i a w^n v_1{}^n)$ has the same meaning as the w of lemma 10. $\rho = \rho_n$, which we shall determine later, has the property that $H_{n,n}(x) >> x^{1-\rho}$ which is true if

$$r_{n,n}(N) = O(N^{\rho})$$

where $r_{k,s}(N)$ denotes the number of representations of N as a sum of s positive kth powers.

§2. *Investigation of an Integral.*

We consider the integral

$$I_N = \int_0^1 T^{n-2} T_1 V^2 S^2 V_w \, e^{-2\pi i \alpha N} d\alpha$$

where, for the interval of integration, we can substitute the interval

$$-\tau^{-1} \leqslant \alpha \leqslant 1 - \tau^{-1}.$$

For every α in the last interval we have the representation

$$\text{(I)} \quad \alpha = \frac{a}{q} + z\,;\ (a, q) = 1\,;\ 0 < q < \tau\,;\ |z| \leqslant \frac{1}{q\tau}.$$

We divide this interval into intervals of two classes. In the first class we include the intervals with

$$\alpha = \frac{a}{q} + z\,;\ (a, q) = 1\,;\ 0 < q \leqslant P^d\,;\ -\frac{1}{\tau} \leqslant z \leqslant \frac{1}{\tau}$$

in the second class the remaining intervals. If

$$\text{A.} \quad 2d < l$$

we can verify without difficulty that the intervals of the first class do not overlap, and they contain all those values of α which may be represented in the form (I) with $q \leqslant P^d$. Therefore every α from the intervals of the second class may be represented in the form (I) with $q > P^d$.

Corresponding to this division of the interval of integration, the integral I_N may be represented as a sum of two terms

$$I_N = H_1 + H_2.$$

§3. *Asymptotical Formula for* H_1.

In order to calculate H_1 we consider the following functions of z

$$\phi = \int_0^P e^{2\pi i z x^n} \, dx\,;\ \phi_1 = \int_0^{3P} e^{2\pi i z x^n} \, dx\,;$$

$$\psi = \int_P^{2P} e^{2\pi i z x^n} \, dx\,;\ \psi_w = \int_R^{2R} e^{2\pi i z w^n x^n} \, dx.$$

Let t run over the set of integers satisfying

$$\text{(II)} \quad -\frac{r}{q} < t \leqslant \frac{P - r}{q}$$

Then we obtain for T,

$$T = \sum_{r=0}^{q-1} \sum_{t} e^{2\pi i \left(\frac{a}{q} + z\right)(qt+r)^n}$$

$$= \sum_{r=0}^{q-1} e^{2\pi i \frac{a}{q} r^n} K_r \text{ where}$$

$$K_r = \sum_{t} e^{2\pi i z q^n \left(t + \frac{r}{q}\right)^n}$$

but the function

$$f(t) = |z|\, q^n \left(t + \frac{r}{q}\right)^n$$

satisfies in the interval (II) the conditions of lemma 3 provided

B. $n - 1 + d < l$.

If this condition is satisfied then by lemma 3,

$$K_r = \int_{\frac{-r}{q}}^{\frac{P-r}{q}} e^{2\pi i z q^n \left(t + \frac{r}{q}\right)^n} dt + O(1).$$

Hence we obtain for T,

(1) $T = \phi B_{a,q} + O(q)$.

In a similar way we find

(2) $T_1 = \phi_1 B_{a,q} + O(q)$,

(3) $V = \psi B_{a,q} + O(q)$;

and finally

$$V_w = \frac{\psi_w}{q} \sum_{r=0}^{q-1} e^{2\pi i \frac{a}{q} w^n r^n} + O(q).$$

But

$$\sum_{v_1} \exp\left(2\pi i \frac{a}{q} v_1^n w^n\right) = \frac{R}{q} \sum_{r=0}^{q-1} \exp\left(2\pi i \frac{a}{q} w^n r^n\right) + O(q).$$

Hence

(4) $V_w = \frac{\psi_w}{R} \sum_{v_1} \exp\left(2\pi i \frac{a}{q} w^n v_1^n\right) + O(q)$.

Further

(5) $S = \sum_{\xi} e^{2\pi i \frac{a}{q} \xi} + O(|z|\, X P^{n-1})$

(6) $e^{-2\pi i N\alpha} = e^{-2\pi i \frac{a}{q} N - 2\pi i z N_0} + O(|z|\, P^{n-\theta})$

We put

(7) $\begin{cases} Z = P & \text{if } |z| \leqslant P^{-n} \\ Z = |z|^{-\nu} & \text{if } |z| \geqslant P^{-n} \end{cases}$

Then we get

$$\phi << Z; \phi_1 << Z; \psi << Z.$$

Therefore by lemma 1 we see that the main term of the right part of the inequalities

(1), (2), (3), (4), (5), (6) is

$$<< Zq^{-\nu}; << Zq^{-\nu}; << Zq^{-\nu}; << R; << X; << 1.$$

The ratios of the remaining terms to the last values are

$$<< Z^{-1} q^{1+\nu} + R^{-1} q + |z| P^{n-\theta} + |z| P^{n-1} << P^{-\theta} (1 + |z| P^n)$$

provided

C. $\theta < 1$.

D. $a \geqslant d + \theta$.

E. $d \leqslant \dfrac{n}{(n+1)} (1-\theta)$.

Hence

$$T^{n-s} T_1 V^s S^s V_w e^{-2\pi i a_N} = F_w E_w + O\,[Z^{n+1} q^{-(1+\nu)} R X^s P^{-\theta} (1 + |z| P^n)]$$

where F_w depends only on z, n, N_0 and

$$(9)\quad E_w = B_{a,q} q^{n+1} \left(\sum_{\xi} e^{2\pi i \frac{a}{q} \xi} \right)^2 \sum_{v_1} e^{2\pi i \frac{a}{q} w^n v_1^n} e^{-2\pi i \frac{a}{q} N},$$

$$(10)\quad E_w << X^s R q^{-1-\nu},$$

$$(11)\quad F_w = \phi^{n-2} \phi_1 \psi^2 \frac{\psi_w}{R} e^{-2\pi i z N_0} << Z^{n+1}.$$

Multiplying by dz and integrating from $z = -\dfrac{1}{\tau}$ to $z = +\dfrac{1}{\tau}$ we find that the part of H_1 corresponding to the interval with any a and q is

$$Q_w E_w + L$$

where Q_w depends only on n, N_0. Now

$$(12)\quad L << X^s R P^{-\theta} q^{-1-\nu} \left(\int_0^{P^{-n}} P^{n+1} dz + \int_{P^{-n}}^{\tau^{-1}} P^n |z|^{-\nu} dz \right)$$

$$<< X^s R P^{-\theta} q^{-1-\nu} \left[P + P^{-l+n+\frac{l}{n}} \right]$$

provided

F. $l < n \quad (\tau \leqslant P^n)$

so

$$\sum_{q=1}^{P^d} \sum_{a} L << X^s\, R P P^{d(1-\nu)} \left\{ P^{-\theta} + P^{-l+\frac{l}{n}+n-1-\theta} \right\} = o\,(X^s R P)$$

provided

G_1. $d(1-\nu) < \theta$

and

$$G_2. \quad d(1-\nu) < l - \frac{l}{n} - n + 1 + \theta.$$

Hence

$$(14)\quad H_1 = Q_w D_w + o\,(X^2RP),$$

$$(15)\quad D_w = \sum_{q=1}^{P^d} \sum_{a} E_w$$

where a runs through all values not exceeding q and prime to it.

§4. *Estimation of* Q_w.

We sum up the equality

$$I_N = H_1 + H_2$$

for all values of N satisfying the condition

$$N_0 - N_0 P^{-\theta} < N \leqslant N_0.$$

The result of summation of the left side is equal to the number of solutions of the inequalities

$$(16)\quad N_1 - N_0 P^{-\theta} < x^n \leqslant N_1$$

where

$$(17)\quad N_1 = N_0 - x_1^n - \cdots - x_{n-2}^n - u - u' - w^n v_1^n,$$

and x runs over the set of values 1, 2, $\cdots$, 3P; every x_i runs over the set 1, 2, $\cdots$, P; u and v_1 are the values described before, and u' takes the same values as u but independently.

Now

$$N_1 - N_0 P^{-\theta} \geqslant N_0 - (n-2)P^n - 2(2P)^n + O(P^{na}) - N_0 P^{-\theta} >> P^n >> N_0$$

provided

H. $\quad a < 1.$

Hence the number of solutions of (16) for any given N_1 is equal to

$$N_1^{\nu} - (N_1 - N_0 P^{-\theta})^{\nu} + O(1) >> \frac{N_0}{N_1^{1-\nu} P^{\theta}} >> P^{1-\theta}$$

so the whole number of solutions of (16) is

$$>> P^{n-2} X^2 P^2 R P^{1-\theta} = X^2 R P^{n+1-\theta}.$$

The part of H_1 corresponding to $q = 1$ is

$$Q_w X^2 R$$

and its summation for all the above values of N is

$$Q_w X^2 R\{N_0 P^{-\theta} + O(1)\}.$$

When $q > 1$ by lemma 4

$$\left| \sum_{N} \exp\left(-2\pi i \frac{a}{q} N\right) \right| < \frac{1}{2}\left(\frac{a}{q}\right)^{-1}.$$

and so by (14) when $q > 1$, the part of $\sum_{N} H_1$ corresponding to such q is

$$<< |Q_w| X^2 R \sum_{q=2}^{P^d} q^{-1-\nu} \sum_{a} \frac{1}{2\left(\frac{a}{q}\right)}$$

$$(20) \quad << |Q_w| X^2 R P^d.$$

It follows that

$$(21) \quad \sum_{N} H_1 = Q_w X^2 R\{N_0 P^{-\theta} + O(1) + O(P^d)\} \sim Q_w X^2 R N_0 P^{-\theta}$$

provided

J. $d < n - \theta$.

In the intervals of the second class

$$\sum_{N} e^{-2\pi i a N} << \frac{1}{(a)} << P^l$$

so

$$(22) \quad \sum_{N} H_2 << P^{n-1} R P^l \int_0^1 \sum_{u,u'} e^{2\pi i(u-u')\alpha} d\alpha$$

$$<< P^{n-1} R P^l P X = P^{n+l} X R$$

$$= o(X^2 R P^{n+1-\theta}) \text{ if}$$

K. $l + \sigma < n - \theta$.

Hence

$$(23) \quad X^2 R P^{n+1-\theta} << Q_w X^2 R N_0 P^{-\theta} + o(X^2 R P^{n+1-\theta})$$

whence

$$(24) \quad Q_w >> P.$$

§5. *Estimation of* D_w.

We shall now define the numbers ξ. Let ζ be the set of numbers not exceeding $\frac{P_1^n}{w^n}$ which are sums of n nth powers $\geqslant 0$. Then the set of numbers ξ is defined by $\xi = w^n \zeta$. It is evident that for any ξ we have $\xi \leqslant P_1^n$. Further for X, the number of ξ's we obtain

$$X >> \left(\frac{P_1^n}{w^n}\right)^{1-\rho} >> P^{(n-1)(1-\rho)} = P^{n-1-(n-1)\rho}.$$

We set

$$(25) \quad \sigma = (n-1)\rho, \textit{ i.e.}, \rho = \frac{\sigma}{n-1}$$

then

$$(26) \quad X >> P^{n-1-\sigma}.$$

We have

$$(27) \quad \Gamma_w = \sum_{N_2} e^{-2\pi i \frac{a}{q} N_2} B_{a,q}^{n+1}$$

where

$$(28)\quad N_2 = N - \xi - \xi' - w^n v_1{}^n \equiv N \pmod{w} \equiv 1 \pmod{w}$$

Therefore

$$(29)\quad D_w = \sum_{N_2} \sum_{q=1}^{P^d} A_q(N_2) = \sum_{N_2} \{c(N_2) + o(1)\} >> X^2R,$$

since $N_2 \equiv 1(w)$ and lemma 10 [we have also used lemma 2 for $t = n + 1$ and the fact that $d(N) = O(N^\epsilon)$ for any $\epsilon > 0$].

Thus we obtain

$$(30)\quad H_1 >> X^2RP.$$

§6. *Estimation of* H_2.

We shall now investigate the sum

$$V_w = \sum_{v_1=R}^{2R-1} e^{2\pi i a w^n v_1{}^n}$$

in an interval of the second class. Every point of such an interval satisfies

$$a = \frac{a}{q} + z, \quad |z| \leqslant \frac{1}{q^\tau}, \quad q \geqslant P^d.$$

It follows that

$$(31)\quad V_w = \sum_{v_1=R}^{2R-1} e^{2\pi i \frac{a}{q} w^n v_1{}^n} + O\left(\frac{RP^{an}}{P^{d+l}}\right).$$

The order term here is $O(P\lambda)$ where

$$(32)\quad \lambda = (n+1)\,a - d - l.$$ The leading term is

$$\sum_{v_1=R}^{2R-1} e^{2\pi i \frac{a'}{q'} v_1{}^n} \text{ where } (a', q') = 1, q' \geqslant \frac{q}{w^n}, q' \leqslant q.$$

By lemma 8 the latter sum is

$$<< R^\epsilon q^\epsilon \left(R^{1-\frac{1}{k}} + Rq^{-\frac{1}{k}} + R^{1-\frac{n}{k}} q^{\frac{1}{k}}\right)$$

$$<< P^\epsilon R\left(P^{-\frac{a}{k}} + P^{-\frac{d}{k}} + P^{\frac{l-an}{k}}\right)$$

$$<< P^\epsilon R\left(P^{\frac{l-an}{k}}\right)$$

if

L. $d < a,\ an - l < d,\ an - l > 0.$

Set

$$(33)\quad \frac{an-l}{k} = \delta > 0.$$

Then from the above we obtain

$$(34)\quad V_w << (RP^{\epsilon-\delta} + P\lambda) << RP^{\epsilon-\delta}$$

if

M. $\lambda < a - \delta$.

Now

$$(35)\quad H_2 << P^{n-1}RP^{\epsilon-\delta}\int_0^1 \sum_{u,u'} e^{2\pi i(u-u')\alpha}\, d\alpha$$

$$<< P^n XRP^{\epsilon-\delta} = o(H_1) = o(X^2PR)$$

if

N. $\sigma < \delta \left(i.e.,\ \rho < \dfrac{\delta}{n-1} = \dfrac{an-l}{n-1}\right)$.

Hence if our conditions A, B, etc., N are satisfied then

$$I_N = H_1 + H_2 = H_1\,[1 + o(1)].$$

Putting $N = N_0$ [this implies $N_0 \equiv 1 (\mathrm{mod}\ w)$] we get

$$(36)\quad I_{N_0} >> H_1 >> X^2RP > 0.$$

Hence for large $N_0 \equiv 1(w)$ we have

$$(37)\quad N_0 = x^n + (x_1^n + \cdots + x_{n-2}^n) + y_1^n + y_2^n + \xi + \xi' + w^n v_1^n$$

= *a sum of* $(3n + 2)$ *nth powers* $\geqslant 0$.

Collecting our conditions we have

A. $2d < l$. B. $n - 1 + d \leqslant l$. C. $\theta < 1$.

D. $a \geqslant d + \theta$. E. $d \leqslant \dfrac{n}{n+1}(1 - \theta)$. F. $l < n$.

G_1. $d(1 - \nu) < \theta$. G_2. $d(1 - \nu) < l - \dfrac{l}{n} - n + 1 + \theta$.

H. $a < 1$. J. $d < n - \theta$. K. $l + \sigma < n - \theta$.

L. $d < a$, $an - l < d$, $an - l > 0$.

M. $\lambda = (n + 1)\, a - d - l < a - \delta \left(\delta = \dfrac{an - l}{K}\right)$. N. $\sigma < \delta$.

All our conditions are satisfied by taking (for large n)

$$a = \frac{l + \frac{d}{2}}{n},\ \delta = \frac{\nu}{6k},\ \sigma = \frac{\nu}{8k},\ l = n - \frac{1}{2},$$

$$\theta = \frac{1}{2} - \nu^2,\ d = \frac{\nu}{3}.$$

The condition $\sigma = \dfrac{1}{n2^{n+2}}$ is the same $\left(\text{since } \rho = \dfrac{\sigma}{n-1}\right)$ as

$$(38)\quad H_{n,n}(x) >> x^{1 - \frac{1}{n(n-1)2^{n+2}}}$$

Hence if this condition is satisfied then every large number $\equiv 1 (\mathrm{mod}\ w)$, where w depends only on n, is a sum of $(3n + 2)$ nth powers $\geqslant 0$. Our result IV is now proved.

THE OCCURRENCE OF FURAN DERIVATIVES IN VOLATILE OILS—II.

α-Clausenan and Di-α-Clausenan.

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and
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The volatile oil from the leaves of *Clausena Willdenovii*, W. and A. has been shown to mainly consist of α-, β- and *di-α-clausenan* belonging to the furan group.[1] The major constituent was α-clausenan. The oil from the leaves grown in another locality was found not to contain any α-clausenan but an isomeric substance, γ-clausenan. As a further supply of α-clausenan in the near future seemed doubtful, it seemed desirable to put on record an account of the experiments that have been done with the limited quantity available.

α-Clausenan like some other furan derivatives gave an addition product with maleic anhydride, having the composition $C_{14}H_{14}O_4$, white crystalline needles melting at 85°. The corresponding acid $C_{14}H_{16}O_5$. $9H_2O$ (m.p. 98°) was obtained as white flakes from water. It lost $7H_2O$ at 110° and the remaining two molecules at 140°. The anhydrous acid melted at 248° and could be directly obtained by recrystallising the hydrated acid from absolute alcohol or ether.

α-Clausenan with aqueous mercuric chloride at room temperature gave a white crystalline solid which did not melt but merely turned yellow at 180°. Its composition was $C_{10}H_{10}O(HgCl)_2$ showing that two molecules of mercuric chloride had reacted.

During oxidation of α-clausenan with an aqueous solution of ferrous sulphate, the furan nucleus was not effected. The reaction product consisted exclusively of a mixture of a primary and a tertiary alcohol of the same formula $C_{10}H_{14}O_2$. On acetylation the mixture of alcohols yielded the original hydrocarbon α-clausenan and an acetate, the former being formed by dehydration of the tertiary alcohol. Both the alcohols and the acetate gave

[1] *Proc. Ind. Acad. Sci.*, 1934, 1, 184.

the Liebermann and the bromine colouration tests[2] showing the presence of the furan nucleus in them. The presence of a grouping $R_1R_2C = CH_2$ is indicated in the side chain giving $R_1R_2C(OH)CH_3$ (tertiary alcohol) and $R_1R_2CHCH_2OH$ (primary alcohol). This was supported by the formation of a ketone $C_9H_{10}O_2$ by oxidation with potassium permanganate. The ketone gave no solid derivatives but gave the colour reactions. Besides the ketone a small quantity of acid was obtained giving an anilide, m.p. 154° too small to be identified.

Dilute nitric acid (d., 1·12) had little action on α-clausenan below 30°. With fuming nitric acid in acetic acid solution, a flocculent pale yellow precipitate was obtained in quantitative yield. It was found to be a nitro-ketone $C_9H_9NO_4$ charring at 130°. With formic acid at 0°C. a resinous product boiling at 240°/2 mm. was formed, no trace of di-α-clausenan being detected. Di-α-clausenan does not combine with maleic anhydride and gives not a tetra- but only a di-mercurial. It is reduced by sodium and alcohol unlike α-clausenan. The significance of these results will be discussed in a subsequent communication.

Experimental.

α-Clausenan used in the following experiments was liberated from ferrocyanic acid addition compound and had the following properties: d_{30}^{30}, 0·9065; n_D^{30}, 1·4722; $(R_L)_D$, 46·02.

Condensation of α-clausenan with maleic anhydride.—Maleic anhydride (7·0 g.) dissolved in dry benzene (50 c.c.) was gradually added to a benzene solution of α-clausenan (9 g.). The solution gradually warmed up and turned yellow. After an hour at laboratory temperature, it was boiled on water-bath for two hours, the solution again becoming colourless. The solvent was distilled off and the oily residue slowly solidified. It was recrystallized from petrol-ether separating as stout needles melting sharply at 85°. It is sparingly soluble in cold water but readily dissolved in boiling water and alkalis. 0·1495 g. required 13·7 c.c. of 0·0885 N alkali giving an equivalent of 123·2 (calc. 123·0). The condensation anhydride rapidly decolorises a solution of bromine in chloroform. But no crystalline addition products of bromine could be isolated due to resinification. It is very soluble in most organic solvents except petrol-ether in which it is sparingly soluble.

Hydrolysis of the anhydride.—The anhydride (2 g.) was dissolved in just the theoretical quantity of 5 per cent. ice-cold aqueous potassium hydroxide and then acidified with ice-cold dilute acetic acid, when an acid (3 g.) separated as white flakes which washed with water and dried *in vacuo* melted at 98°.

[2] *Loc. cit.*

The use of mineral acids and higher temperature gave a resinous product which on recrystallisation gave a diminished yield of the pure acid. The acid (m.p. 98°; 0·2868 g.) lost water (0·0868 g.) at 110° and further lost (0·0238 g.) at 140° giving an anhydrous acid melting at 248°. The hydrated acid (0·1370 g.) required for neutralisation alkali (7·2 c.c.; 0·0885 N) giving an equivalent of 214; $C_{14}H_{16}O_5$. $9H_2O$ gives an equivalent of 213. It loses 7 molecules of water at 110°, the remaining two molecules at 140°. Analysis of the anhydrous acid: C, 67·8; H, 5·5; $C_{14}H_{16}O_5$ requires C, 68·3; H, 5·7 per cent. The acid (0·1297 g.) required alkali (9·7 c.c.; 0·0885 N) for neutralisation an equivalent of 132·4 (calc. 132). The anhydrous acid was also obtained by recrystallising the hydrated acid from absolute alcohol or ether when it was obtained in soft glistening needles, m.p. 248°.

Oxidation of α-clausenan with ferrous sulphate; α-clausenyl alcohol.—α-Clausenan (23 c.c.) was shaken for 8 hours with a saturated solution of ferrous sulphate (70 c.c.). The oily layer was removed, dried over magnesium sulphate and distilled when it had the following properties: b.p. 88–89°/28 mm.; d_{30}^{30}, 0·9432; n_D^{30}, 1·4777; C, 73·0; H, 8·5; $C_{10}H_{14}O_2$ requires C, 72·3; H, 8·5. This did not form any addition compound with ferro- or ferri-cyanic acids but gave the Liebermann's test and bromine colouration showing the presence of the furan ring. The acetyl value was 212 indicating only partial acetylation. By Sudborough-Zerewitinoff method[3] 0·1376 g. gave 22·4 c.c. at 24°C. and 683 mm. showing hydroxyl, 10·6 per cent. $C_{10}H_{14}O_2$ requires 10·2 per cent. This indicated that the oxidation product was a monohydroxylic compound and that the furan ring was intact. On fractionation of the product at 28 mm. it was found to be a mixture, the following results being obtained:

TABLE I.

No.	B. P.	d_{30}^{30}	n_D^{30}
1	−88·5°	0·9430	1·4775
2	88·5−89	0·9436	1·4778
3	89−89·5	0·9443	1·4778

By acetylation of the mixture of alcohols and distillation at 30 mm., the following fractions were obtained:—

[3] *J. C. S.*, 1904, **85**, 933; *Ber.*, 1907, **40**, 2023.

a	−90°	0·9046	1·4730
b	90—93	0·9050	1·4732
c	93—98	0·9319	1·4682
d	98—100	0·9524	1·4684

Fractions *a* and *b* on distillation over sodium had the following properties: b.p. 104°/53 mm.; d_{30}^{30}, 0·9067; n_D^{30}, 1·4722. It combined with ferro-cyanic acid and was identical in every respect with α-clausenan.

Fraction d: Analysis: C, 69·8; H, 7·8; $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7. On saponification with alcoholic potash it gave an alcohol having the following properties: b.p. 89–90°/30 mm.; n_D^{30}, 1·4779; d_{30}^{30}, 0·9441 in good agreement with fraction 3, Table I. This primary alcohol has been called α-clausenyl alcohol. This could be quantitatively acetylated and gave a liquid phthalic ester when treated with phthalic anhydride in benzene solution. The re-acetylated product had the following properties: b.p. 98–102°/30 mm.; n_D^{30}, 1·4683; d_{30}^{30}, 0·9522. The proportion of the two alcohols formed during oxidation with ferrous sulphate varied in different experiments. The α-clausenyl alcohol as well as the acetate resinified far more rapidly than α-clausenan itself.

Oxidation of α-clausenan with potassium permanganate.—To α-clausenan (10 c.c.) in acetone (100 c.c.) potassium permanganate (20 g.) was gradually added in small quantities, the temperature being maintained between 0–5° C. The mixture was poured into water and manganese dioxide filtered off. The neutral product had the following properties: b.p. 95–96°/55 mm.; d_{30}^{30}, 0·9285; n_D^{30}, 1·4531; C, 71·2; H, 7·0; $C_9H_{10}O_2$ requires C, 72·0; H, 6·7. It reacted quantitatively with hydroxylamine, giving a liquid oxime, no solid ketonic derivatives being obtained. The filtrate was concentrated and acidified when a small quantity of resinous product was obtained. It yielded an anilide, m.p. 154° but the quantity available being small it was not further investigated.

Action of nitric acid on α-clausenan.—Dilute nitric acid (d., 1·12) has little action at laboratory temperature, tarry products being formed, when the temperature was raised. With fuming nitric acid, better results were obtained. To α-clausenan (6·4 g.) dissolved in glacial acetic acid (32 c.c.) and cooled in a freezing mixture fuming nitric acid (d., 1·52; 4 c.c.) dissolved in glacial acetic acid (20 c.c.) was gradually added under vigorous stirring

according to Marquis.[4] On pouring into water a micro-crystalline yellow solid separated (9·0 g.). It is soluble in chloroform, ethyl acetate, acetone, ether, benzene and insoluble in petrol-ether and water. It dissolves in alkalis and is purified by solution in chloroform and reprecipitation with petrol and then chars at 130° C. Analysis : C, 54·9 ; H, 4·9 ; N, 7·4 ; $C_9H_9NO_4$ requires C, 55·1 ; H, 4·6 ; N, 7·2. It formed a semicarbazone which did not melt below 350° ; N, 21·0 ; $C_{10}H_{12}O_4N_4$ requires N, 22·22.

Mercuration of α-clausenan.—To a solution of mercuric chloride (2 g.) and sodium acetate (4 g.) in water (50 c.c.) cooled by ice was added α-clausenan (1·5 g.) in alcohol (8 c.c.).[5] A solid began separating after a few minutes, the solution turning slightly red. The oil gradually disappeared after 48 hours. The pale-buff coloured precipitate was filtered off and dried and was purified by extracting with large quantities of hot acetone. The colourless crystalline solid (0·6 g.) thus obtained did not melt but became yellow at 180°. It turned black with mineral acids, alkalis and sodium carbonate. Mercury was estimated after solution in strong nitric acid and titration against standard thiocyanate solution ; Hg, 65·4 ; $C_{10}H_{11}O.HgCl$ requires Hg, 52·3, $C_{10}H_{10}O(HgCl)_2$ requires Hg, 64·9 thus showing that it was a di-chloro-mercury derivative.

Di-α-Clausenan.

The product used in the experiments below had the following properties : b.p. 188°/7 mm. ; d_{30}^{30}, 1·048 ; n_D^{30}, 1·5468.

Action of fuming nitric acid.—To di-α-clausenan (5 g.) dissolved in glacial acetic acid (30 c.c.) cooled in a freezing mixture, a glacial acetic acid (20 c.c.) solution of fuming nitric acid (4 c.c.) was gradually added under stirring during an hour and then poured over ice. A yellow solid similar to the one from α-clausenan separated. It charred at 140° and dissolved in most organic solvents except petrol-ether. It was purified by reprecipitating it from a chloroform solution ; C, 55·1 ; H, 5·0 ; N, 7·4 ; $C_{18}H_{18}N_2O_8$ requires C, 55·1 ; H, 4·6 ; N. 7·2.

Mercuration of di-α-clausenan.—To mercuric chloride (4 g.) and sodium acetate (8 g.) dissolved in water (100 c.c.) was added di-α-clausenan (3 g.) in alcoholic solution. A solid separated in comparatively poor yield and after purification with acetone weighed 0·4 g. A resin was formed as a subsidiary product, which could be removed by washing the mercurial with chloroform in which the resin was found to be very soluble. The mercurial turned yellow at 150°. Analysis : Hg, 53·7 ; $C_{20}H_{22}O_2(HgCl)_2$ requires Hg, 52·4.

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[4] *Ann. Chem. Phys.*, 1905, 4(viii), 196.

[5] *J. Amer. Chem. Soc.*, 1933, **55**, 3303.

Di-α-clausenan showed no tendency to combine with maleic anhydride. Unlike α-clausenan it could be reduced by sodium and ethyl alcohol, a product having the following properties being obtained: b.p. 100–101°/4 mm.; d_{30}^{30}, 0·9354; n_D^{30}, 1·4906.

Summary.

The condensation product of α-clausenan and maleic anhydride and the corresponding acid have been described. Di-chloromercury derivatives have been prepared both from α-clausenan and di-α-clausenan. By oxidation with ferrous sulphate, a primary alcohol (α-clausenyl alcohol, $C_{10}H_{14}O_2$) is formed along with an isomeric tertiary alcohol which is easily dehydrated to α-clausenan. Two positions, one of which is α, appear to be free in the furan nucleus of α-clausenan. The formation of a ketone $C_9H_{10}O_2$ and a nitro-ketone $C_9H_9NO_4$ from it indicates the presence of a terminal methylene group.

REDUCTION OF THE —CHOH. CCl_3 GROUP.

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In continuation of the work on the reduction of the — CHOH. CCl_3 group, the condensation products of chloral with mono-methyl, mono-ethyl, dimethyl and diethyl anilines[1] were reduced with zinc and acetic acid. The condensation product of chloral with methyl-benzyl-aniline which is new, was also reduced. The reduction products were found to contain the group $-CH_2CHCl_2$. The nitroso-derivatives of the mono-alkyl products were reduced to the corresponding hydrazines.

Experimental.

Preparation of the chloral condensation products.—Bossneck's method[2] was modified in that the bases were kept with chloral at room temperature for 36 hours, or were heated at 50° for 10–15 hours ; the condensation product was isolated as the hydrochloride. The free base was obtained by treating the hydrochloride with ammonia.

Reduction of the condensation products.—The base suspended in glacial acetic acid was treated with zinc dust below 50°. The reduction product separated from the filtered reaction mixture on dilution. A further yield of the reduction product was obtained by washing the residual mixture of zinc acetate and zinc dust with water, and then extracting the reduction product from the zinc residue with alcohol. The condensation products from diethyl and methyl-benzyl-anilines were reduced in the form of their hydrochlorides. The filtrate from the reaction mixture was then diluted and treated with ammonia, and the oil which separated, extracted with ether.

p-(ββ-dichloro-ethyl)-mono-methyl-aniline, $CH_3HNC_6H_4CH_2CHCl_2$, separated from alcohol or acetic acid in needles m.p. 77°. (Found : Cl, 34·7%; $C_9H_{11}N.Cl_2$ requires Cl, 34·8%.)

[1] Bossneck, *Ber.*, 1885, **18**, 1519; 1886, **19**, 368; 1887, **20**, 3193; 1888, **21**, 782, 783.

[2] *Loc. cit.*

The benzoyl derivative crystallised from dilute alcohol in needles, m.p. 130°. (Found : Cl, 23·0%; $C_{16}H_{15}ON.Cl_2$ requires Cl, 23·0%.)

p-(ββ-dichloro-ethyl)-mono-ethyl-aniline, $C_2H_5HN.C_6H_4.CH_2.CHCl_2$ separated from dilute acetic acid in plates, m.p. 73°. (Found : Cl, 32·4%; $C_{10}H_{13}N.Cl_2$ requires Cl, 32·6%.)

The benzoyl derivative crystallised from alcohol in plates, m.p. 75°. (Found : Cl, 21·9%; $C_{17}H_{17}ON.Cl_2$ requires Cl, 22·0%.)

p-(ββ-dichloro-ethyl)-dimethyl-aniline, $(CH_3)_2NC_6H_4.CH_2.CHCl_2$ crystallised from dilute acetic acid in feathery leaflets, m.p. 76°. (Found : Cl, 32·7%; $C_{10}H_{13}N.Cl_2$ requires Cl, 32·6%.)

The picrate crystallised from alcohol in needles, m.p. 138°. [Found : picric acid 50·5%[3]; calculated for $(C_{10}H_{13}NCl_2)\{C_6H_2(OH)(NO_2)_3\}$, 51·2%.]

p-(ββ-dichloro-ethyl)-diethyl-aniline, $(C_2H_5)_2N.C_6H_4.CH_2.CHCl_2$ is an oil. *The picrate* separated from CCl_4 in leaflets, m.p. 140°. [Found : picric acid, 58·9 %; calculated for $(C_{12}H_{17}N.Cl_2)_2\{C_6H_2(OH)(NO_2)_3\}_3$, 58·3 %. [Found : Cl, 12·2 %; $(C_{12}H_{17}N.Cl_2)_2\{C_6H_2(OH)(NO_2)_3\}_3$ requires Cl, 12·0 %.]

p-(βββ-trichloro-α-ethylol)-methyl-benzyl-aniline hydrochloride $C_6H_5\overset{CH_3}{\underset{CH_2}{<}}>N.C_6H_4CHOHCCl_3.HCl$ crystallised from alcohol acidified with HCl; decomp. 150°.

The base crystallised from alcohol in plates m.p. 85° with decomposition. (Found : Cl, 31·0%; $C_{16}H_{16}ON.Cl_3$ requires Cl, 30·9%.)

p-(ββ-dichloro-ethyl)-methyl-benzyl-aniline $C_6H_5\overset{CH_3}{\underset{CH_2}{<}}>N.C_6H_4.CH_2.CHCl_2$ is an oil. *The picrate* crystallised from CCl_4 in plates, m.p. 132°. [Found : picric acid 51·6%; calculated for $(C_{16}H_{17}N.Cl_2)_3\{C_6H_2(OH)(NO_2)_3\}_4$, 50·9%.]

The nitroso-derivative of p-(ββ-dichloro-ethyl)-mono-methyl-aniline, $CH_3(NO)NC_6H_4CH_2CHCl_2$, separated when a mixture of *p*-(ββ-dichloro-ethyl)-mono-methyl-aniline (2 g.) in alcohol and sodium nitrite (3 g.) in water was treated at 0° with dilute HCl ; yield 2 g. ; (87 % theory). It crystallised from alcohol in clusters of needles, m.p. 87°. (Found : Cl, 30·3%; $C_9H_{10}ON_2Cl_2$ requires Cl, 30·5 %.)

Nitroso-derivative of p-(ββ-dichloro-ethyl)-mono-ethyl-aniline $C_2H_5NON.C_6H_4CH_2CHCl_2$.

A mixture of *p*-(ββ-dichloro-ethyl)-mono-ethyl-aniline (2 g.) in alcohol and sodium nitrite (3 g.) in water was treated at 0° with dilute HCl, and the

[3] *Cf.* Houben Weyl: *Die Arbeiten der Methodischen die Chemie*, Vol. I, p. 218.

nitroso-derivative extracted with ether. It crystallised from alcohol in needles, m.p. 50°; yield 2 g. (Found: Cl, 28·7%; $C_{10}H_{12}ON_2.Cl_2$ requires Cl, 28·8%.)

α-methyl-α-p-(ββ-dichloro-ethyl-phenyl)-hydrazine hydrochloride,

$$\begin{matrix} CH_3 \\ NH_2 \end{matrix}\!> N.C_6H_4.CH_2.CHCl_2.HCl.$$

Reduction of the nitroso-derivative, $\begin{matrix} CH_3 \\ NO \end{matrix}\!> N.C_6H_4CH_2CHCl_2.$

The nitroso-derivative (2 g.) suspended in alcohol (14 g.) and acetic acid 50% (8 g.) was shaken with zinc dust (5 g.) for 3 hours at 15°. The filtrate was diluted, neutralised with ammonia, and extracted with ether; hydrogen chloride was passed through the ether extract, when the hydrochloride separated; it crystallised in plates from dilute alcohol acidified with HCl. (Found: Cl, 41·5%; $C_9H_{13}N_2.Cl_3$ requires Cl, 41·7%.)

α-ethyl-α-p-(ββ-dichloro-ethyl-phenyl)-hydrazine hydrochloride,

$$\begin{matrix} C_2H_5 \\ NH_2 \end{matrix}\!> N.C_6H_4.\ CH_2.\ CHCl_2.HCl.$$

Reduction of the nitroso-derivative $\begin{matrix} C_2H_5 \\ NO \end{matrix}\!> N.C_6H_4.\ CH_2.\ CHCl_2.$

The nitroso-derivative (2 g.) suspended in alcohol (14 g.) and acetic acid 50 % (8 g.) was reduced with zinc dust (5 g.) in the same way as the corresponding mono-methyl compound. The hydrazine hydrochloride crystallised in feathery plates from dilute alcohol acidified with HCl. (Found: Cl, 39·6%; $C_{10}H_{15}N_2Cl_3$ requires Cl, 39·8%.)

α-methyl-α-p-(ββ-dichloro-ethyl-phenyl)-hydrazone of benzaldehyde

$C_6H_5CH : \begin{matrix} CH_3 \\ N \end{matrix}\!> N.C_6H_4.\ CH_2.\ CHCl_2$ was obtained by treating a mixture of the hydrazine hydrochloride (2 g.) and benzaldehyde (1 g.) with dilute acetic acid. It crystallised from dilute alcohol in plates, m.p. 150°. (Found: Cl, 23·1%; $C_{16}H_{16}N_2Cl_2$ requires Cl, 23·1%.)

α-methyl-α-p-(ββ-dichloro-ethyl-phenyl)-hydrazone of glucose

$$\begin{matrix} CH : \begin{matrix} CH_3 \\ N \end{matrix}\!> N.C_6H_4.\ CH_2.\ CHCl_2. \\ (\dot{C}HOH)_4 \\ CH_2OH \end{matrix}$$

Ammonia was added to the hydrazine hydrochloride (1 g.) and the free base extracted with ether; glucose (·7 g.) was added to the ethereal solution; the residue from the ethereal solution was crystallised from alcohol when plates

m.p. 165° were obtained. (Found: Cl, 18·5%; $C_{15}H_{22}O_5N_2Cl_2$ requires Cl, 18·6%.)

α-ethyl-α-p-(ββ-dichloro-ethyl-phenyl)-hydrazone of benzaldehyde,

$$C_6H_5CH : N\!<^{C_2H_5}\!> N.C_6H_4.CH_2.CHCl_2$$

prepared in the same way as the corresponding mono-methyl compound crystallised from alcohol in plates, m.p. 110°. (Found: Cl, 22·0%; $C_{17}H_{18}N_2.Cl_2$ requires Cl, 22·1%.)

A CONTRIBUTION TO THE PROBLEM OF TWO SAMPLES.

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1. *Introductory.*

The hypothesis, say H, that two samples of observations of a single variable have been drawn from the same population may be tested in a variety of ways. If there are strong grounds for believing that the populations sampled are approximately normal, then the only possible difference of importance will be between their means a_1 and a_2 or standard deviations σ_1 and σ_2; it is customary, therefore, to test separately for the significance of differences between (1) the sample variances σ_1 and σ_2 and (2) the sample means a_1 and a_2. If, however, both tests are on the border line of significance it may be difficult to decide what conclusions to draw; for this and other reasons there appear to be certain advantages in the availability of a single comprehensive test of the hypothesis of a common origin for the two samples. Such tests are frequently applied in statistical analysis; if the two samples contain many observations the hypothesis may be tested by applying the χ^2 test to the two series of grouped frequencies and so obtaining a single criterion to judge the probability of H. Again when a number of samples are available and it is wished to test whether the means in the several sampled populations are identical, a single test (whether in z or η^2 form) is applied rather than a separate test for each pair of samples.

J. Neyman and E. S. Pearson have discussed the use of such comprehensive tests in a number of problems. They have pointed out that in comparing two alternative tests they should in the first place be made equivalent, that is to say, adjusted so that in both cases the risk of rejection of H when it is true is the same; consideration should then be given to the relative efficiency of the two tests in rejecting the hypothesis when some alternative is true. They have shown that in certain cases there is a single test associated with a best critical region which is more efficient than any other from this last point of view.[1] In other cases no test with a best critical region common for all alternative hypotheses exists, but they have

[1] *Phil. Trans. Roy. Society, Series A*, 1933, **231**.

suggested the use of the principle of likelihood in picking out a test that may be described as associated with a good critical region.[2]

In the present problem they have suggested the use of a test[3] based on a criterion L_1 defined below. The main object of this paper is to discuss the derivation and use of Tables of 5% and 1% probability levels for this criterion, but as a preliminary point it is of interest partly on theoretical grounds to compare this form of test with two alternative comprehensive tests of the same hypothesis.

2. Comparison of L_1 test with two alternative two-sample tests.

If two samples of size n_1 and n_2 have been drawn randomly from two normal populations, then we may use as criteria to test separately the significance of the difference (1) between variances and (2) between means

$$1. \quad u = \frac{n_1 s_1^2}{n_1 s_1^2 + n_2 s_2^2} \qquad \ldots\ldots \qquad (1)$$

$$2. \quad t = \frac{\bar{x}_1 - \bar{x}_2}{\sqrt{n_1 s_1^2 + n_2 s_2^2}} \sqrt{\frac{n_1 n_2 (n_1 + n_2 - 2)}{n_1 + n_2}} \qquad \ldots\ldots \qquad (2)$$

where $\bar{x}_1$ and $\bar{x}_2$ are the means of two samples and

$$n_1 s_1^2 = \sum_{i=1}^{n_1} (x_i - \bar{x}_1)^2 ; \quad n_2 s_2^2 = \sum_{i=1}^{n_2} (x_i - \bar{x}_2)^2$$

If the population variances are the same, then the sampling distribution of u is

$$f_1(u) = \text{constant } u^{\frac{1}{2}(n_1 - 1) - 1} (1 - u)^{\frac{1}{2}(n_2 - 1) - 1} \qquad \ldots\ldots \qquad (3)$$

If both the population means and variances are the same and we write $n_1 + n_2 = N$

$$f_2(t) = \text{constant} \left(1 + \frac{t^2}{N - 2}\right)^{-\frac{N-1}{2}} \qquad \ldots\ldots \qquad (4)$$

Neyman and Pearson's criterion is

$$L_1 = \left(\frac{s_1}{s_0}\right)^{\frac{2n_1}{N}} \left(\frac{s_2}{s_0}\right)^{\frac{2n_2}{N}} = \frac{N}{(n_1)^{\frac{n_1}{N}} (n_2)^{\frac{n_2}{N}}} \frac{u^{\frac{n_1}{N}} (1 - u)^{\frac{n_2}{N}}}{\left(1 + \frac{t^2}{N - 2}\right)} \qquad \ldots\ldots \qquad (5)$$

where $s_0^2 = \frac{\sum_{i=1}^{N} (x_i - \bar{x}_0)^2}{N}$, $\bar{x}_0$ being the mean of the combined sample of $N = n_1 + n_2$ observations.

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[2] *Biometrika*, **20A**, pp. 175–240 and 264–294.

[3] On the Problem of Two Samples (1930); On the Problem of k Samples (1931); *Bulletin de L'academie Polonaise des Sciences, Series A, Sciences Mathematiques.*

Fig. 1 is a diagram having co-ordinate axes t and u. The oval contour represents a member of (5) for which $n_1 = n_2 = 15$ and $L = \cdot 8028$, which has been so chosen that the chance is $\cdot 05$ of a point (t, u) falling outside the curve, if the hypothesis H is true. That is to say, if in drawing a sample of 15 from each of two normal populations, it is decided to reject H whenever the point (t, u) falls outside this contour, we shall reject H when in fact the populations have the same mean and standard deviations, 5 times in 100.

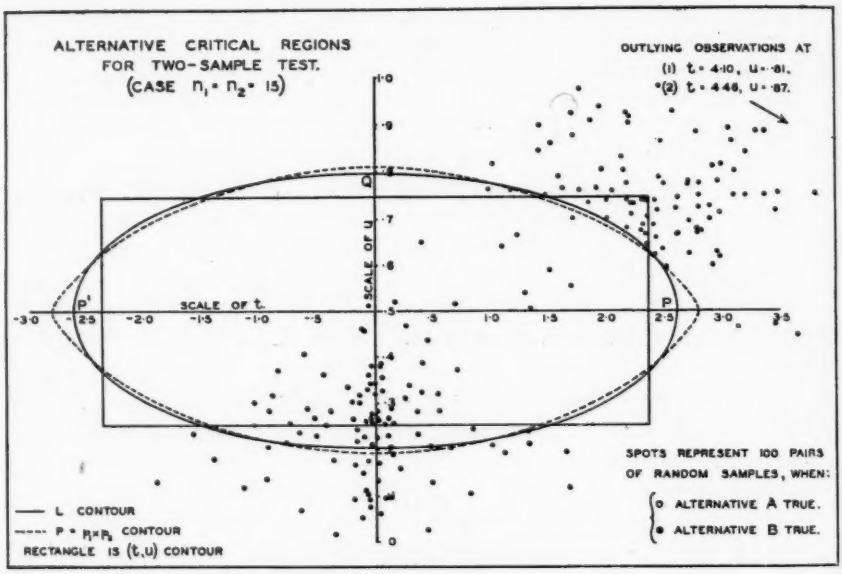

FIG. 1.

We may now use two further alternative contours:

(1) Decide to reject H unless both $u_1 \leqslant u \leqslant u_2$ and $t_1 \leqslant t \leqslant t_2$, *i.e.*, reject H when (t, u) lies outside a rectangle such as that shown in the figure. To make the test equivalent to the previous one, the limits must be chosen so that only 5% of possible sample points fall outside the rectangle if H be true. There will be an infinite number of ways of choosing these limits; in the present instance the limits for u and t are chosen in such a way that the chance of rejection of the hypothesis H_1 when it is true, is equal to the

chance of rejection of H_2 when it is true.[4] If ϵ denotes this chance of rejection, then it follows that the chance of falling inside the rectangle is $\cdot 95 = (1 - \epsilon)^2$, so that $\epsilon = \cdot 02532$.

(2) A third alternative test may be obtained on the lines suggested by R. A. Fisher[5] and K. Pearson.[6] If we write for the case $n_1 = n_2$

$$\left.\begin{aligned} p_1 &= \int_0^u f_1(u)du \quad \text{if } u \leqslant \tfrac{1}{2} \\ p_1 &= \int_u^1 f_1(u)du \quad \text{if } u > \tfrac{1}{2} \end{aligned}\right\} \quad .. \quad .. \quad .. \quad (6)$$

and

$$\left.\begin{aligned} p_2 &= \int_{-\infty}^{t} f_2(t)dt \quad \text{if } t \leqslant 0 \\ p_2 &= \int_{t}^{\infty} f_2(t)dt \quad \text{if } t > 0 \end{aligned}\right\} \quad .. \quad .. \quad .. \quad (7)$$

the criterion suggested is

$$P = p_1 \times p_2 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (8)$$

The region of rejection is that for which P is less than some specified value. The contour in the (t, u) field equivalent to that determined in the other two tests can be readily found from (8) on substituting for P its 5% point given by

$$P_{.05} = e^{-\frac{1}{2}\chi^2_{\cdot 05}} = \cdot 0087.$$

It is drawn as a dotted curve in the figure and differs in the present instance, when $n_1 = n_2$, only slightly from the L contour. It is likely that when $n_1 \neq n_2$ the two contours may differ much more but the case is not considered in this paper.

Having now obtained these equivalent contours associated with the use of these three criteria, it is of interest to consider their relative efficiency in rejecting the hypothesis H when the populations sampled are in fact different.

Since it can be shown[7] that there can be in this case no best critical region common for all alternatives to H, it may be expected that for some

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[4] The hypotheses H_1 and H_2 are identical with those considered by Neyman and Pearson in their paper "On the Problem of Two Samples". H_1 is the hypothesis that the samples have come from some two normal populations with a common variance and H_2 is the hypothesis that the samples have come from populations with a common mean, it being assumed that the populations have the same variance.

[5] *Statistical Methods for Research Workers*, Fourth Edition, p. 97.

[6] *Biometrika*, 1933, **25**, p. 379.

[7] The author has succeeded in proving this rigorously but as the proof extends over several pages it is not given here.

alternatives one criterion will be more efficient, for other alternatives a second and so on. That this is the case is shown in the diagram, where results are given for two series of samplings from populations not satisfying the conditions of the hypothesis.

	Population 1	Population 2
Alternative A.		
Mean ..	0·0	7·25
S.D. ..	10·0	5·75
Alternative B.		
Mean ..	0·0	0·0
S.D ..	10·0	5·75

100 pairs of samples of 15 were drawn in each case and the points (t, u) were plotted. It will be seen that the oval contours contain less circles and more dots than the rectangle. This means that while the L_1 test and also the $(P = p_1 \times p_2)$ test are more likely than the (t, u) test to detect the fact that the sampled populations are different when these populations are as in A, the reverse is the case when the two populations are as in B. It is clear that there is here a matter for further theoretical investigation and the problem for the moment may be left with two questions. If there is no test with a common best critical region for all alternative hypotheses, on what principle can we choose from among other possible alternative tests? Will this principle be found to lead to the likelihood or L_1 criterion, which in many problems already considered appears at any rate to satisfy our intuitional requirements?

3. *The Distribution of* L_1.

Suppose that the samples Σ_1, Σ_2 have been drawn at random from some normal populations with means α_1 and α_2 and standard deviations σ_1 and σ_2 respectively. If the hypothesis that Σ_1 and Σ_2 belong to the same normal populations be true then they must have been drawn from a common population with mean $= \alpha$ and standard deviation $= \sigma$; and we know that the frequency function for the simultaneous variations in $\bar{x}_1$, $\bar{x}_2$, s_1 and s_2 is given by

$$\{\bar{x}_1,\ \bar{x}_2,\ s_1,\ s_2\} = \text{const.}\ (s_1)^{n_1-2}\ (s_2)^{n_2-2}\ e^{-\frac{n_1(\bar{x}_1-\alpha)^2 + n_2(\bar{x}_2-\alpha)^2 + n_1 s_1^2 + n_2 s_2^2}{2\sigma^2}} \quad .. \quad (9)$$

My aim will be to transform the variables and integrate for certain of them until we are left with the frequency function of two variables in terms of which the value of L_1 can be expressed. Substituting first

$$\bar{x}_2' = \bar{x}_2 - \alpha \text{ and } \zeta = \bar{x}_1 - \bar{x}_2 \quad .. \quad .. \quad .. \quad .. \quad (10)$$

we obtain the probability law of $\bar{x}_2'$, ζ, s_1 and s_2

$$f\{\bar{x}_2', \zeta, s_1, s_2\} = \text{const. } (s_1)^{n_1-2}\,(s_2)^{n_2-2}\,e^{-\frac{n_1 s_1^2 + n_2 s_2^2}{2\sigma^2}} \times$$

$$e^{-\frac{1}{2\sigma^2}\left\{(n_1+n_2)\left[\bar{x}_2' + \frac{n_1\zeta}{n_1+n_2}\right]^2 + \frac{n_1 n_2}{n_1+n_2}\zeta^2\right\}} \quad .. \quad (11)$$

Integrating with respect to $\bar{x}_2'$ between the limits $-\infty$ and $+\infty$ and substituting

$$s_0^2 = \frac{n_1 s_1^2 + n_2 s_2^2}{n_1 + n_2} + \frac{n_1 n_2}{(n_1+n_2)^2}\zeta^2 \quad .. \quad .. \quad .. \quad (12)$$

we obtain

$$f\{s_0, s_1, s_2\} = \text{const. } \frac{(s_1)^{n_1-2}(s_2)^{n_2-2}\,e^{-\frac{n_1+n_2}{2\sigma^2}s_0^2}}{\left[1 - \frac{n_1\left(\frac{s_1}{s_0}\right)^2 + n_2\left(\frac{s_2}{s_0}\right)^2}{n_1+n_2}\right]^{\frac{1}{2}}} \quad .. \quad .. \quad (13)$$

Lastly putting $s_1 = s_0 x$ and $s_2 = s_0 y$ .. .. (14)

and integrating for s_0 between the limits 0 and ∞, we get

$$f\{x, y\} = \text{const. } \frac{(x)^{n_1-2}\,(y)^{n_2-2}}{\sqrt{1 - \frac{n_1x^2 + n_2y^2}{n_1+n_2}}} \quad .. \quad .. \quad .. \quad (15)$$

It follows from (5) and (14) that

$$\mathrm{L}_\iota = (x)^{\frac{2n_1}{N}}\,(y)^{\frac{2n_2}{N}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (16)$$

Whence we obtain

$$f\{x, \mathrm{L}_\iota\} = \text{const. } \frac{x^{2\left(\frac{n_1}{n_2}-1\right)}\,\mathrm{L}_\iota^{\frac{N}{2}-\frac{N}{2n_2}-1}}{\sqrt{\mathrm{N}x^{\frac{2n_1}{n_2}} - n_1 x^{\frac{2n_1}{n_2}+2} - n_2\mathrm{L}_\iota^{\frac{N}{n_2}}}} \quad .. \quad .. \quad (17)$$

Therefore

$$f(\mathrm{L}_\iota) = \text{const. } \mathrm{L}_\iota^{\frac{N}{2}-\frac{N}{2n_2}-1}\int_a^b \frac{x^{2\left(\frac{n_1}{n_2}-1\right)}}{\sqrt{\mathrm{N}x^{\frac{2n_1}{n_2}} - n_1 x^{\frac{2n_1}{n_2}+2} - n_2\mathrm{L}_\iota^{\frac{N}{n_2}}}}\,dx \quad .. (18)$$

where a, b denote the real roots of

$$\mathrm{N}x^{\frac{2n_1}{n_2}} - n_1 x^{\frac{2n_1}{n_2}+2} - n_2\mathrm{L}_\iota^{\frac{N}{n_2}} = 0 \quad .. \quad .. \quad .. \quad (19)$$

When $n_1 = n_2 = n$, equation (18) may be written as

$$f(\mathrm{L}_\iota) = \text{const. } \mathrm{L}_\iota^{n-2}\int_a^b \frac{dx}{\sqrt{(x^2-a^2)(b^2-x^2)}} \quad .. \quad .. \quad (20)$$

where a and b are now given by

$$\left.\begin{aligned} a &= \frac{1}{\sqrt{2}}\left\{\sqrt{1+L_r} - \sqrt{1-L_r}\right\} \\ \text{and } b &= \frac{1}{\sqrt{2}}\left\{\sqrt{1+L_r} + \sqrt{1-L_r}\right\} \end{aligned}\right\} \quad .. \quad .. \quad .. \quad (21)$$

On substituting $x^2 = a^2\cos^2\phi + b^2\sin^2\phi$ .. .. .. (22)

in (20) and using (21) we obtain

$$f(L_r) = \text{const.} \frac{L_r^{n-2}}{\sqrt{1+L_r}\left(1+\sqrt{\frac{1-L_r}{1+L_r}}\right)} \int_0 \frac{d\phi}{\sqrt{1 - \frac{4\sqrt{\frac{1-L_r}{1+L_r}}}{\left(1+\sqrt{\frac{1-L_r}{1+L_r}}\right)^2}\sin^2\phi}} \quad .. \quad (23)$$

It will be noticed that the integral in equation (23) is an elliptic integral of the first order with modulus equal to $\sqrt{\frac{4\sqrt{\frac{1-L_r}{1+L_r}}}{\left(1+\sqrt{\frac{1-L_r}{1+L_r}}\right)^2}}$. The modulus appears to be very complex. I shall therefore try to connect this elliptic integral with another having a simple modulus.

Denote $\sqrt{\frac{1-L_r}{1+L_r}}$ by small k. Then the elliptic integral can be written as

$$\int_0^{\frac{\pi}{2}} \frac{d\phi}{\sqrt{1 - \frac{4k}{(1+k)^2}\sin^2\phi}} \quad .. \quad .. \quad .. \quad .. \quad (24)$$

Substituting in (24)

$$2\phi = \theta + \sin^{-1}(k\sin\theta) \quad .. \quad .. \quad .. \quad .. \quad (25)$$

we have

$$\int_0^{\frac{\pi}{2}} \frac{d\phi}{\sqrt{1 - \frac{4k}{(1+k)^2}\sin^2\phi}} = (1+k)\int_0^{\frac{\pi}{2}} \frac{d\theta}{\sqrt{1-k^2\sin^2\theta}} \quad .. \quad (26)$$

the latter being the elliptic integral with modulus k. Hence on evaluating the constant, (23) may be written as

$$f(L_r) = \frac{4\,\Gamma\left(n-\frac{1}{2}\right)\Gamma\left(\frac{n}{2}\right)}{\pi\Gamma(n-1)\Gamma\left(\frac{n-1}{2}\right)} \frac{L_r^{n-2}}{\sqrt{1+L_r}} \int_0^{\frac{\pi}{2}} \frac{d\theta}{\sqrt{1-k^2\sin^2\theta}} \quad .. \quad (27)$$

where

$$k^2 = \frac{1-L_r}{1+L_r}.$$

This expression for the distribution of L_r is more simple and elegant than the one given in equation (23). It is of considerable interest to see how this

form can readily be obtained by using relation (5) which may be written as

$$L = L_1 \times L_2 \quad .. \quad .. \quad .. \quad .. \quad .. \quad (28)$$

where $$L_1 = \frac{N}{(n_2)^{\frac{n_2}{N}} (n_1)^{\frac{n_1}{N}}} u^{\frac{n_1}{N}} (1-u)^{\frac{n_2}{N}} \quad .. \quad .. \quad .. \quad (29)$$

and $$L_2 = \left(1 + \frac{t^2}{N-2}\right)^{-1} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (30)$$

For this purpose it is essential to obtain the distribution of L_1, which can be easily done as follows :

The probability law of s_1^2 and s_2^2 is given by

$$f\{s_1^2, s_2^2\} = \text{const.} \; (s_1^2)^{\frac{n_1-3}{2}} (s_2^2)^{\frac{n_2-3}{2}} e^{-\frac{1}{2\sigma^2}(n_1 s_1^2 + n_2 s_2^2)} \quad .. \quad (31)$$

Substituting

$$\sqrt{\frac{n_1}{2}} \frac{s_1}{\sigma} = r \cos\beta \; ; \; \sqrt{\frac{n_2}{2}} \frac{s_2}{\sigma} = r \sin\beta \quad .. \quad .. \quad (32)$$

and integrating w.r.t. r between the limits 0 and ∞ we obtain

$$f(\beta) = \text{const.} \; (\cos\beta)^{n_1-2} (\sin\beta)^{n_2-2} \quad .. \quad .. \quad .. \quad (33)$$

It follows from (29) and (32) that

$$L_1 = N \left\{ \frac{(\cos^2\beta)^{n_1}}{n_1^{n_1}} \frac{(\sin^2\beta)^{n_2}}{n_2^{n_2}} \right\}^{\frac{1}{N}} \quad .. \quad .. \quad .. \quad .. \quad (34)$$

On substituting (34) in (33) we get

$$f(L_1) = \text{const.} \; L_1^{\frac{N}{2}-1} \{\sin\beta \cos\beta \; (n_2 \cos^2\beta - n_1 \sin^2\beta)\}^{-1} \; .. \quad (35)$$

where β may be written in terms of L_1 from (34). When $n_1 = n_2$, (35) may be written on evaluating the constant, as

$$f(L_1) = \frac{2\Gamma\left(\frac{n}{2}\right)}{\Gamma\left(\frac{n-1}{2}\right) \Gamma\left(\frac{1}{2}\right)} (L_1^2)^{\frac{n}{2}-1} (1 - L_1^2)^{-\frac{1}{2}} \quad .. \quad .. \quad (36)$$

It will be noticed that L_1^2 is distributed in Pearson type I curve. This distribution has been recently deduced independently by Mr. Nayer from the distribution of u by using relation (29).[8]

The distribution of L_2 which can be easily deduced from the t distribution by using (30) is given by

$$f(L_2) = \frac{\Gamma(n-\frac{1}{2})}{\Gamma(n-1)\,\Gamma(\frac{1}{2})} (L_2)^{n-2} (1 - L_2)^{-\frac{1}{2}} \quad .. \quad .. \quad .. \quad (37)$$

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[8] 'Practical Application of Neyman and Pearson's L_1 test.' Thesis for the degree of M.Sc. in the University of London, 1934.

It follows from (28) that the distribution of L_r will be that of $L_{r_1} L_{r_2}$. From (36) and (37) we get

$$f(L_{r_1} L_{r_2}) = \frac{2\,\Gamma(\frac{n}{2})\,\Gamma(n-\frac{1}{2})}{\pi\,\Gamma(\frac{n-1}{2})\,\Gamma(n-1)} L_{r_1}^{n-2}(1-L_{r_1}^2)^{-\frac{1}{2}} L_{r_2}^{n-2}(1-L_{r_2})^{-\frac{1}{2}} \quad (38)$$

Substituting $L_{r_1} = \frac{L}{L_{r_2}}$ in (38) and integrating w.r.t. L_{r_2} between the limits L_r and 1, we have

$$f(L_r) = \frac{4}{\pi} \frac{\Gamma(n-\frac{1}{2})\,\Gamma(\frac{n}{2})}{\Gamma(n-1)\,\Gamma(\frac{n-1}{2})} \frac{L_r^{n-2}}{\sqrt{1+L_r}} K \quad .. \quad .. \quad .. \quad (39)$$

where K represents the elliptic integral

$$\int_0^{\frac{\pi}{2}} \frac{d\theta}{\sqrt{1-k^2\sin^2\theta}} \quad .. \quad .. \quad .. \quad .. \quad .. \quad (40)$$

It will be noticed that (39) and (27) are identical.

4. Methods of Evaluating the Probability Integral of L_r.

(*a*) *The general case.*

To calculate the probability that L_r exceeds a given value L_{r_0} it is necessary to integrate (15) so that

$$(x)^{\frac{2n_1}{N}}(y)^{\frac{2n_2}{N}} > L_{r_0} \text{ and } n_1x^2+n_2y^2 \leqslant N \quad .. \quad .. \quad (41)$$

Solving for y we get $y = \sqrt{\frac{N-n_1x^2}{n_2}}$ the upper limit of y

and $y = \left(\frac{L}{x^{\frac{2n_1}{N}}}\right)^{\frac{N}{2n_2}}$ the lower limit of y.

If the corresponding roots of x be denoted by b and a then

$$p(L_r > L_{r_0}) = \sqrt{N}\,C \int_a^b dx \int_{\left(\frac{L_r}{x^{\frac{2n_1}{N}}}\right)^{\frac{N}{2n_2}}}^{\sqrt{\frac{N-n_1x^2}{n_2}}} \frac{x^{n_1-2}\,y^{n_2-2}}{\sqrt{N-n_1x^2-n_2y^2}}\,dy \quad .. \quad (42)$$

where

$$C = \frac{4(n_1)^{\frac{n_1-1}{2}}(n_2)^{\frac{n_2-1}{2}}\Gamma\left(\frac{n_1+n_2-1}{2}\right)}{\Gamma(\tfrac{1}{2})\,(n_1+n_2)^{\frac{n_1+n_2-2}{2}}\,\Gamma\left(\frac{n_1-1}{2}\right)\Gamma\left(\frac{n_2-1}{2}\right)} \quad .. \quad (43)$$

Substituting

$$y = \sqrt{\frac{\xi(N-n_1x^2)}{n_2}} \quad .. \quad .. \quad .. \quad .. \quad (44)$$

we obtain

$$p(L_i > L_{i0}) = \frac{\sqrt{N}\,C}{2(n_2)^{\frac{n_2-1}{2}}}\int_a^b x^{n_1-2}(N-n_1x^2)^{\frac{n_2}{2}-1}\,dx\int_{\xi_1}^1 \xi^{\frac{n_2}{2}-1}(1-\xi)^{-\frac{1}{2}}\,d\xi \quad .. \quad (45)$$

where

$$\xi_1 = \left(\frac{L_i^{\frac{N}{2n_2}}}{x^{\frac{n_1}{n_2}}}\right)^2 \times \frac{n_2}{N-n_1x^2} \quad .. \quad .. \quad .. \quad .. \quad (46)$$

Substituting further

$$\frac{n_1}{N}x^2 = \eta$$

$$p(L_i > L_{i0}) = \frac{4}{\sqrt{\pi}}\,\frac{\Gamma\left(\frac{N-1}{2}\right)}{\Gamma\left(\frac{n_1-1}{2}\right)\Gamma\left(\frac{n_2-1}{2}\right)}\int_{\frac{n_1}{N}a^2}^{\frac{n_1}{N}b^2}\eta^{\frac{n_1-3}{2}}(1-\eta)^{\frac{n_2-1}{2}}\,d\eta \times$$

$$\int_{\xi_1}^1 \xi^{\frac{n_2}{2}-1}(1-\xi)^{-\frac{1}{2}}\,d\xi \quad .. \quad .. \quad (47)$$

which can be evaluated on using the Tables of the Incomplete Beta Function.[9]

(*b*) *Case* $n_1 = n_2$.

The simple method of quadrature may be used with advantage when $n_1 = n_2 = n$. The main difficulty is the evaluation of the ordinates of L_i-frequency curve. Equation (39) shows that this depends on the evaluation of the elliptic integral K.

[9] Edited by Karl Pearson.

There are several Tables in use of the elliptic integrals. The Tables[10] by L. M. Milne Thomson, particularly, suit here well. In these Tables the values of K are given for all values of k^2 differing by ·01. Interpolation into the Tables, however, becomes more and more difficult as k^2 increases. In such cases, the following method of evaluating K was adopted :—

$$\text{Let} \qquad \epsilon = \tfrac{1}{2}\,\frac{1-(1-k^2)^{\frac{1}{4}}}{1+(1-k^2)^{\frac{1}{4}}} \qquad .. \qquad .. \qquad .. \qquad .. \qquad .. \quad (48)$$

then the nome q is given by

$$q = \epsilon + 2\epsilon^5 + 15\epsilon^9 + 150\epsilon^{13} + 1707\epsilon^{17} + 20910\epsilon^{21} + ... \qquad .. \quad (49)$$

The series (49) enables us to calculate the value of q, corresponding to the desired value of k^2. By means of these values of q the function

$$\vartheta = 1 + 2q + 2q^4 + ... \qquad .. \qquad .. \qquad .. \qquad .. \quad (50)$$

was calculated. The value of K is then easily obtained by multiplying ϑ^2 by $\frac{\pi}{2}$.

(*c*) *An approximate method.*

This method, suggested by Neyman and Pearson in their paper, consists in assuming Pearson type I curve to represent the probability law of L_ϵ and obtaining the probability integral from the Tables of the Incomplete Beta Function. That is to say

$$f(L_\epsilon) = \frac{\Gamma(m_1+m_2)}{\Gamma(m_1)\Gamma(m_2)}\, L_\epsilon^{m_1-1}\,(1-L_\epsilon)^{m_2-1} \qquad .. \qquad .. \qquad .. \quad (51)$$

represents the probability law of L_ϵ, where the values of m_1 and m_2 are given by

$$m_1 = \frac{\mu_1'(\mu_1'-\mu_2')}{\mu_2'-\mu_1'^2}; \quad m_2 = \frac{(1-\mu_1')\,(\mu_1'-\mu_2')}{\mu_2'-\mu_1'^2} \qquad .. \qquad .. \quad (52)$$

μ_1' and μ_2' being the first two moment coefficients of L_ϵ about zero. It was, however, found in the present case that the values of m_2 differed only very slightly from unity and consequently the lower 5% and 1% values of L_ϵ were immediately available from the following relations:

$$L_{\epsilon 5\%} = (\cdot 05)^{\frac{1}{m_1}} \text{ and } L_{\epsilon 1\%} = (\cdot 01)^{\frac{1}{m_2}} \qquad .. \qquad .. \qquad .. \quad (53)$$

The lower limits are used because the criterion L_ϵ is of such form that the hypothesis tested becomes less and less likely as L_ϵ decreases from 1 towards 0.

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[10] *Proceedings of the London Mathematical Society*, **33**.

5. The Calculation of the Tables and an Illustration of their Use.

Before using these simple relations in forming the Tables it was essential to examine the approximations involved. This was accomplished by comparing the values of $L_5\%$ and $L_1\%$ at (1) $n_1 = n_2 = 5$, 12, 20, 60 and (2) $n_1 = 5$, $n_2 = 15$, found by using (53) with those obtained by using the exact methods (*a*) and (*b*). The agreement between the two sets of values of L was found exact to three decimal places. Consequently the relation (53) was employed in forming the Tables. Tables I and II give these values for a number of different values of n_1 and n_2. Interpolation into the Tables for any pair of values of n_1 and n_2 less than 120 will be found fairly easy.

When either n_1 or n_2 exceeds 120, the percentage values of L can be obtained from the Tables of χ^2. It has been shown by Neyman and Pearson that if n_1 and n_2 are sufficiently large and we write $L_{\frac{1}{2}}^{N} = e^{-\frac{1}{4}\chi^2}$, then the frequency distribution of χ is given by

$$f(\chi) = \chi\, e^{-\frac{1}{4}\chi^2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots \quad (54)$$

It follows that for large values of n_1 and n_2, approximations to the probability integral of L can be obtained from the Tables of the χ^2 integral. Using Fisher's Tables of χ^2, we find that the 5% and 1% values of χ^2 for two degrees of freedom are 5·991 and 9·210 respectively. Hence we get

$$L_{\cdot 05} = e^{-\frac{5\cdot 991}{n_1+n_2}} \text{ and } L_{\cdot 01} = e^{-\frac{9\cdot 210}{n_1+n_2}} \qquad \ldots\ldots\ldots\ldots \quad (55)$$

On comparing the values of L obtained by this method with the exact ones, it was found that when n_1 and n_2 both exceeded 70 the agreement was excellent and differed only in the fourth place. The agreement, however, begins to fall off if the two samples are extremely unequal in size but it is very rarely that we may have to test two samples when one of them is thrice as large or larger than the other. I conclude therefore that if the average size of the two samples is sufficiently large and both the samples are of about the same size then $L_{\cdot 05}$ and $L_{\cdot 01}$ can be obtained by direct use of relation (55).

One very interesting point comes out of the above discussion. Equation (55) shows that the value of L does not depend on the values of n_1 and n_2 individually but on $n_1 + n_2$, or put in another way, on the average size of sample. This means that whatever be n_1 and n_2, so long as they are large and not very unequal, the sampling distribution of L is that which would be obtained if n_1 and n_2 were both equal to their average value $\frac{1}{2}(n_1+n_2)$. The importance of this result is considerably enhanced by the fact that it is

TABLE I.

5 per cent. values of L.

n_2 \ n_1	5	6	7	8	9	10	12	15	20	24	30	40	60	120	∞
5	·442	·487	·522	·553	·579	·602	·641	·687	·742	·773	·808	·848	·892	·942	1·000
6	·487	·527	·559	·587	·611	·632	·667	·709	·758	·787	·820	·856	·897	·945	1·000
7	·522	·559	·589	·615	·637	·656	·688	·726	·772	·798	·828	·862	·901	·947	1·000
8	·553	·587	·615	·638	·658	·675	·705	·740	·782	·807	·835	·868	·905	·948	1·000
9	·579	·611	·637	·658	·676	·692	·720	·752	·792	·815	·841	·872	·907	·949	1·000
10	·602	·632	·656	·675	·692	·707	·733	·763	·800	·822	·847	·876	·910	·950	1·000
12	·641	·667	·688	·705	·720	·733	·755	·781	·813	·833	·856	·882	·913	·952	1·000
15	·687	·709	·726	·740	·752	·763	·781	·803	·830	·847	·866	·890	·918	·954	1·000
20	·742	·758	·772	·782	·792	·800	·813	·830	·852	·865	·881	·900	·924	·956	1·000
24	·773	·787	·798	·807	·815	·822	·833	·847	·865	·876	·890	·906	·928	·958	1·000
30	·808	·820	·828	·835	·841	·847	·856	·866	·881	·890	·901	·914	·933	·960	1·000
40	·848	·856	·862	·868	·872	·876	·882	·890	·900	·906	·914	·925	·940	·962	1·000
60	·892	·897	·901	·905	·907	·910	·913	·918	·924	·928	·933	·940	·950	·967	1·000
120	·942	·945	·947	·948	·949	·950	·952	·954	·956	·958	·960	·962	·967	·975	1·000
∞	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000

TABLE II. *1 per cent. values of* I$_x$.

n_2 \ n_1	5	6	7	8	9	10	12	15	20	24	30	40	60	120	∞
5	·286	·331	·369	·402	·432	·459	·505	·562	·632	·673	·721	·776	·839	·913	1·000
6	·331	·374	·410	·441	·469	·494	·537	·589	·654	·692	·737	·788	·847	·917	1·000
7	·369	·410	·444	·473	·499	·522	·563	·611	·671	·707	·749	·797	·853	·919	1·000
8	·402	·441	·473	·501	·525	·547	·584	·629	·686	·720	·759	·804	·857	·921	1·000
9	·432	·469	·499	·525	·548	·568	·603	·645	·698	·730	·767	·810	·861	·923	1·000
10	·459	·494	·522	·547	·568	·587	·620	·660	·709	·739	·774	·815	·864	·925	1·000
12	·505	·537	·563	·584	·603	·620	·649	·684	·728	·755	·787	·824	·870	·927	1·000
15	·562	·589	·611	·629	·645	·660	·684	·714	·751	·775	·802	·836	·877	·930	1·000
20	·632	·654	·671	·686	·698	·709	·728	·751	·781	·800	·822	·850	·886	·933	1·000
24	·673	·692	·707	·720	·730	·739	·755	·775	·800	·816	·835	·860	·892	·935	1·000
30	·721	·737	·749	·759	·767	·774	·787	·802	·822	·835	·852	·872	·899	·939	1·000
40	·776	·788	·797	·804	·810	·815	·824	·836	·850	·860	·872	·888	·909	·943	1·000
60	·839	·847	·853	·857	·861	·864	·870	·877	·886	·892	·899	·909	·924	·949	1·000
120	·913	·917	·919	·921	·923	·925	·927	·930	·933	·935	·939	·943	·949	·962	1·000
∞	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000	1·000

easily generalised for the problem of k samples and is applicable alike to all the three criteria L_ϵ, L_{ϵ_1} and L_{ϵ_2}.

EXAMPLE: Two samples of skulls containing 15 and 13 individuals respectively give the following value for the mean and the standard deviation of the Cephalic Index. It is wished to test whether these two samples come from populations with a common Cephalic Index.

$$\text{Sample (1) } n_1 = 15\,;\ \bar{x}_1 = 76{\cdot}4067\,;\quad s_1^2 = 6{\cdot}6806$$
$$\text{Sample (2) } n_2 = 13\,;\ \bar{x}_2 = 73{\cdot}7077\,;\quad s_2^2 = 6{\cdot}9238$$

Substituting these values in

$$s_0^2 = \frac{n_1 s_1^2 + n_2 s_2^2}{n_1 + n_2} + \frac{n_1 n_2}{(n_1 + n_2)^2}(\bar{x}_1 - \bar{x}_2)^2$$

we obtain

$$s_0^2 = 8{\cdot}6053\,;\ \frac{s_1^2}{s_0^2} = {\cdot}7763\,;\ \text{and}\ \frac{s_2^2}{s_0^2} = {\cdot}8046.$$

Since

$$\begin{aligned} L_\epsilon \log L_\epsilon &= \frac{n_1}{N}\log\left(\frac{s_1^2}{s_0^2}\right) + \frac{n_2}{N}\log\left(\frac{s_2^2}{s_0^2}\right) \\ &= \tfrac{15}{28}(\bar{1}{\cdot}89003) + \tfrac{13}{28}(\bar{1}{\cdot}90558) = \bar{1}{\cdot}89725 \end{aligned}$$

we have $L_\epsilon = {\cdot}789.$

Now to obtain the $L_{\epsilon\cdot 05}$ we shall have to interpolate into the Table II for $n_1 = 15$ and $n_2 = 13$. We have from the column headed $n_1 = 15$

n_2	$L_{\epsilon\cdot 05}$	$\delta^2 L_{\epsilon\cdot 05}$
20	·830	
15	·803	5
12	·781	4
10	·763	

The values 20, 15, 12 and 10 are in harmonic progression. Taking $u = 60/n_2$ as the new argument the value of u corresponding to $n_2 = 20$, 15, 12 and 10 becomes 3, 4, 5 and 6 respectively and the problem reduces to interpolating for $u = \frac{60}{13} = 4{\cdot}6154$ from the Table above which gives the values of $L_{\epsilon\cdot 05}$ corresponding to equidistant values of u. Actually on using Everett's simplified formula for interpolation it is found that $L_{\epsilon\cdot 05} = {\cdot}788$. The observed value is therefore very near to the 5% level. Since this is somewhat exceptional we shall do well to enquire whether the significance is due to difference in means or standard deviations of the populations. This leads us to apply the t and z tests. On using these it is found $t = 2{\cdot}633$ and $z = {\cdot}0234$, while the corresponding 5% values are 2·056 and ·4649 respectively. The value of t is thus definitely significant while that of z is

not, suggesting thereby that it was very unlikely that the two series of skulls came from populations with a common mean Cephalic Index.

6. Sensitiveness of I_t *Test when applied to Non-Normal Data.*

It will be recalled that the application of I_t test presupposes that the samples are drawn from some normal population. Actually, however, we may sometimes deal with non-normal data and consequently it is necessary to know whether our test becomes invalid in this case.

There are two ways in which the I_t test may become invalid when the variation is non-normal.

(*a*) It will cease to be the most appropriate test.

(*b*) Its sampling distribution will no longer have the form given in equation (18).

It is difficult to measure the precise effect of (*a*) and (*b*) ; for, the task of devising tests appropriate to every possible form of non-normal variation and constructing the tables is an impossible one. It is possible, however, to obtain experimentally some idea regarding the validity of I_t test when applied to non-normal data. This could be accomplished by testing the goodness of fit of the I_t distribution for samples drawn from a series of non-normal populations. Table III gives the types of populations which have been considered. The types have been represented by curves of the Pearson system.

TABLE III.

Population curves	β_1	β_2	Standard deviation in terms of grouping unit
Type II	0	2·5	6·32
Type VII	0	4·1	5·67
Type III	0·2	3·3	5·00
Type I	1·0	3·8	12·37

The results of sampling carried out from these populations were kindly given to me by Dr. E. S. Pearson. It will be seen from the Table that one of the four populations is very skew, one is very leptokurtic while the remaining two are moderately non-normal.

Tables IV and V compare the observed distributions of I_t obtained from these experimental populations with the expected values calculated from the

TABLE IV.

$n_1 = 10$; $n_2 = 20$.

Limits of L	Normal Theory Frequencies	Frequencies in Samples from Experimental Populations			
		(0·0, 2·5)	(0·0, 4·1)	(0·2, 3·3)	(1·0, 3·8)
·99—1·00	25·2	31	26	25	30
·98— ·99	23·0	25	15	18	17
·97— ·98	18·8	19	18	21	15
·96— ·97	17·2	22	12	22	15
·95— ·96	15·2	17	19	19	6
·94— ·95	13·3	11	6	11	11
·93— ·94	11·7	9	14	8	14
·92— ·93	10·2	4	8	5	8
·91— ·92	8·9	10	11	9	7
·90— ·91	7·7	5	12	4	7
·89— ·90	6·7 } 12·6	8 } 14	3 } 12	9 } 17	1 } 8
·88— ·89	5·9 }	6 }	9 }	8 }	7 }
·87— ·88	5·1 } 9·5	7 } 13	6 } 11	3 } 11	5 } 12
·86— ·87	4·4 }	6 }	5 }	8 }	7 }
·85— ·86	3·8 }	4 }	1 }	3 }	5 }
·84— ·85	3·3 } 10·0	2 } 9	2 } 5	2 } 8	3 } 11
·83— ·84	2·9 }	3 }	2 }	3 }	3 }
·82— ·83	2·5 }	1 }	4 }	6 }	4 }
·81— ·82	2·1 } 8·0	3 } 5	3 } 12	3 } 12	4 } 12
·80— ·81	1·8 }	0 }	3 }	.. }	2 }
·79— ·80	1·6 }	1 }	2 }	3 }	2 }
·78— ·79	1·3 }	2 }	3 }	1 }	4 }
·77— ·78	1·1 }	1 }	3 }	1 }	2 }
·76— ·77	1·0 }	1 }	2 }	.. }	4 }
·75— ·76	·8 }	.. }	1 }	.. }	2 }
·74— ·75	·7 }	.. }	.. }	2 }	2 }
·73— ·74	·6 } 8·7	1 } 6	2 } 19	.. } 10	2 } 27
·72— ·73	·5 }	.. }	.. }	2 }	.. }
·71— ·72	·4 }	1 }	1 }	.. }	1 }
·70— ·71	·4 }	.. }	1 }	.. }	2 }
Less than ·70	1·9 }	.. }	6 }	4 }	8 }
Totals	200·0	200	200	200	200
Mean L	·9305	·9383	·9161	·9265	·9078
σ_L	·0648	·0573	·0769	·0690	·0860
χ^2	..	12·4	30·7	14·4	54·0
P(χ^2)	..	·5744	·0025	·4211	·000004

law (27). The number of pairs of samples used are 200 when the sizes of two samples are 10 and 20 and also when they are each equal to 20. In the

TABLE V.

$n_1 = n_2 = 20$.

Limits of L	Normal Theory Frequencies	Frequencies in Samples from Experimental Populations			
		(0·0, 2·5)	(0·0, 4·1)	(0·2, 3·3)	(1·0, 3·8)
·99—1·00	34·2	33	28	30	31
·98— ·99	28·6	34	20	24	28
·97— ·98	23·8	18	18	31	25
·96— ·97	20·0	21	20	18	23
·95— ·96	16·6	13	14	18	15
·94— ·95	13·8	16	15	14	10
·93— ·94	11·4	16	16	10	4
·92— ·93	9·4	12	8	11	11
·91— ·92	7·8 } 14·2	4 } 14	6 } 16	7 } 12	8 } 13
·90— ·91	6·4 }	10 }	10 }	5 }	5 }
·89— ·90	5·2 } 9·6	4 } 11	5 } 9	4 } 6	4 } 5
·88— ·89	4·4 }	7 }	4 }	2 }	1 }
·87— ·88	3·6	4	3	5	4
·86— ·87	2·8 } 8·8	.. } 5	4 } 15	3 } 13	1 } 10
·85— ·86	2·4	1	8	5	5
·84— ·85	2·0	3	3	3	6
·83— ·84	1·6	2	4	3	5
·82— ·83	1·2	1	4	2	4
·81— ·82	1·0	1	1	1	..
·80— ·81	·8 } 9·6	.. } 7	1 } 21	.. } 13	1 } 25
·79— ·80	·7	..	3	1	..
·78— ·79	·6	..	1	1	1
·77— ·78	·5	..	1	..	..
Less than ·77	1·2	..	3	2	8
Totals	200·0	200	200	200	200
Mean L	·9491	·9521	·9342	·9459	·9395
σ_L	·0484	·0404	·0572	·0498	·0605
χ^2	..	8·4	25·8	9·0	34·4
P(χ^2)	..	·6767	·0070	·6219	·0009

lower part of the Tables are given the values of mean L, σ_L and the results of applying the (P, χ^2) test for goodness of fit.

The following points are suggested by an examination of the Tables :

(i) The agreement of the observed frequencies of L with those expected is satisfactory in the case of moderately non-normal distributions (0, 2·5) ; (·2, 3·3) ; while it is far from satisfactory in the case of the extremely skew or leptokurtic distributions.

(ii) A comparison of the means and the standard deviations of L_1 suggests the same conclusions.

(iii) A comparison of the detailed frequencies shows that there is a tendency for too many low values of L_1 to occur when the variation markedly differs from the normal. This is of particular interest because it is this tail of the sampling distribution which is of importance in tests of significance. In Table VI a comparison is made at about the levels $p_L = \cdot 05$ and $p_L = \cdot 02$ of the frequencies, theoretical and observed, of obtaining the value of L_1 less than the value indicated in the third column of the Table.

TABLE VI.

Frequencies in two-hundred samples less than a given value of L_1.

Size of Samples		Value of L less than	Expected on Normal Theory	Observed in Experimental sampling from the given distributions			
n_1	n_2			(0·0, 2·5)	(0·0, 4·1)	(0·2, 3·3)	(1·0, 3·8)
10	20	·800	10·3	7	21	13	29
		·740	3·8	2	8	6	13
20	20	·850	9·6	7	21	13	25
		·810	3·8	0	9	4	10

The observed frequencies are of course subject to random sampling errors but it appears from Table VI that the difference (observed − expected frequency) increases both as the population β_1 and β_2 increase. For the moderately skew population (0·2, 3·3), however, little error appears to arise.

Thus on the whole it will be found that there is little to fear in the application of L_1 test to data of moderately skew nature.

7. *Summary.*

(*a*) The use of a single comprehensive test of the hypothesis H of a common origin for the two samples is discussed. It is shown that a single best test of the hypothesis H does not exist. A comparison between L_1 and two alternative two sample tests is made, which illustrates how the use of one test may be more efficient than the other with regard to a given alternative.

(*b*) The sampling distribution of L_s is obtained. It is found that the distribution involves an elliptic function of the first order when the samples are of equal size.

(*c*) Tables of the 5% and 1% levels of probability for L_s have been provided.

(*d*) Finally the question whether the test is suitable for application to non-normally distributed material is discussed. It is found that unless the distribution is extremely non-normal the test may be applied in practice.

In conclusion I like to express my thanks to Professor E. S. Pearson and Dr. J. Neyman for their advice and criticism while this paper was being prepared.

A Note on the Relation of the L_s, u *and* t *Tests. By Prof. E. S. Pearson.*

It will perhaps not be regarded as out of place if I add a few remarks to what Mr. Sukhatme has written regarding the alternative L_s and (t, u) tests, particularly in view of difficulty that arises in the interpretation of his skull measurement example. Here the sample point lies on the 5% L_s-contour but outside the 1% t-contour, and the case $n_1 = 15$, $n_2 = 13$ is very closely similar to that illustrated in Mr. Sukhatme's diagram with $n_1 = n_2 = 15$. If the reader turns to this diagram he will notice that a sample point (t, u) lying at P (or P') on the 5% L_s-contour is extremely divergent judged from the point of view of t. In fact since for this point $t = 2 \cdot 62$, the chance of a more divergent positive value is less than $\cdot 01$.[11] Similarly a sample at Q (or Q')[12] is very exceptional (if H be true) judged from the point of view of u. If, however, in testing H we were to use the 5% level of the t-test whenever a sample point were in the direction of P or P', the 5% level of the u (or z) test whenever in the direction of Q or Q' and the L_s-contour only when the point was diagonally placed, we should in fact be using a far more stringent test than we may have intended. Following this procedure we should in the long run of experience be rejecting H when true in considerably more than 5% of samples, a result which follows because we are selecting the criterion with which to test H *after* we examined the sample data.

The real justification of using the t-test would appear to be that there were strong grounds for believing σ_1 to be equal to or nearly equal to σ_2, so that it was only of interest to test H_2.[13] The statistician who while believing

[11] Note that in the skull example $t = 2.63$ and $u = 0.53$.

[12] Q' is the point where the curve cuts the u-axis nearer $u = 0$, and is not marked in the figure.

[13] See foot-note (4) for definition of H_2.

he was testing the hypothesis H, rejected this hypothesis when a sample point occurred near P or P′ would probably be influenced, perhaps unconsciously, by *a priori* considerations as to the likelihood of the certain alternatives. He would, for instance, be perhaps influenced by the common experience that population means α_1 and α_2 frequently differ while their standard deviations σ_1 and σ_2 are practically the same. Or from another point of view he would be regarding it as more important to detect a difference in means than a difference in standard deviations.[14]

In this action he might well be justified from the practical viewpoint, and Mr. Sukhatme's illustration serves to bring out admirably the difficulties connected with *a priori* probability that arise in an attempt to choose a good critical region for testing a statistical hypothesis when no best critical region exists. To recognise the difficulties is, however, an important first step towards meeting them. The intuitional basis upon which the practical statistician chooses the test he will employ is very frequently sound, but sometimes it is demonstrably at fault. As the principles of choice become more clearly outlined and generally understood these faults will cease, and we shall be left at any rate with a choice among good tests even if there is no agreement as to the best.

[14] The question of the influence of *a priori* knowledge on the contours of the sampling test was referred to by Dr. Neyman and myself in the paper introducing the likelihood criterion (*Biometrika*, **20A**, p. 190). The same point and a further one concerning the relative importance of different errors in judgment were discussed later in a paper entitled "The Testing of Statistical Hypothesis in Relation to Probabilities *a priori*." *Proc. Camb. Phil. Soc.*, **29**, pp. 492-510.

A STUDY OF THE BENZOIN REACTION—V.

The Effect of Inhibitors on the Benzoin Reaction.

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Received November 7, 1935.

In previous papers from this laboratory[1] it has been shown that pure potassium cyanide and pure benzaldehyde react in absence of water to give benzoin. Two concurrent reactions take place: a fast homogeneous autocatalytic reaction which can only occur in presence of benzoin, and a slow heterogeneous reaction which is subject to inhibition by compounds such as KCl, NaCl, KI and quinol. This paper comprises a study of the effect of sulphur, carbon disulphide, thiobenzaldehyde, iodine and quinone on the reaction between pure benzaldehyde and pure solid potassium cyanide.

Experimental and Discussion of Results.

The analytical methods and the general technique were as described in Part I of the present series. Merck's purest benzaldehyde and Kahlbaum's purest cyanide dried as described before, were used. The inhibitors added were purified as described below, and were either weighed and added to the benzaldehyde, or, when the quantities required were below 0·0005 gm., standard solutions in benzaldehyde were prepared and diluted to the required strength. It was confirmed by experiment that the effect of these standard solutions on the reaction did not alter after keeping for fixed periods. All the inhibitors used were soluble in benzaldehyde at 100° C. in the proportions employed.

The results with sulphur are given in detail; with the other compounds a summary only is included. In order to obtain consistent results with sulphur, it was found necessary to dissolve it in carbon disulphide and, after filtration, to recover the sulphur by evaporation. The residue was distilled five times under 2 mm. pressure. The product was found to give reproducible results which were not affected by further distillation. Table I shows the

[1] Parts I, II and III, *J. Phys. Chem.*, 1935, **39**, 727, 901, 907; Part IV, *Proc. Ind. Acad. Sci.*, 1935, **2**, 483.

results obtained at 100° C. by shaking 10 gms. benzaldehyde and 1, 2 and 3 gms. KCN with various amounts of purified sulphur.

TABLE I.

Time in hours	Grams Yield of Benzoin with										
	1 gm. KCN				2 gms. KCN			3 gms. KCN			
	Gms. Sulphur added										
	0·001	0·002	0·004	0·008	0·001	0·002	0·004	0·001	0·002	0·004	0·008
1	1·79	1·33	0·96	0·50	2·53	2·16	1·88	2·93	2·63	2·40	1·86
2	6·52	5·86	5·26	4·92	7·38	6·94	6·54	7·56	7·35	7·09	6·96
3	7·96	7·78	7·67	7·08	8·30	8·33	8·32	8·51	8·49	8·42	8·37
4	—	—	—	8·24	—	—	—	—	—	—	—

The following table gives the yields obtained under the above conditions, without addition of sulphur.

TABLE II.

Time in hours	1 gm. KCN	2 gms. KCN	3 gms. KCN
1	2·72 gms.	3·47 gms.	3·85 gms.
2	7·12 ,,	7·55 ,,	8·01 ,,
3	8·01 ,,	8·55 ,,	8·86 ,,
4	8·34 ,,	8·80 ,,	9·18 ,,

Fig. 1 shows the curves obtained with 1 gm. KCN and various amounts of sulphur. The curves obtained with 2 and 3 gms. of KCN are similar in nature. It was found that the autocatalytic portions of all the curves have a constant slope practically independent of the amount of potassium cyanide or sulphur. As explained in Part I, this indicates that the homogeneous autocatalytic reaction is dependent only on the amount of potassium cyanide dissolved in the reaction mixture. This amount is independent of the total quantity of KCN present and is unaffected by the sulphur; the inhibition of the reaction is due to the sulphur affecting the rate of the heterogeneous reaction by being adsorbed on the solid potassium cyanide.

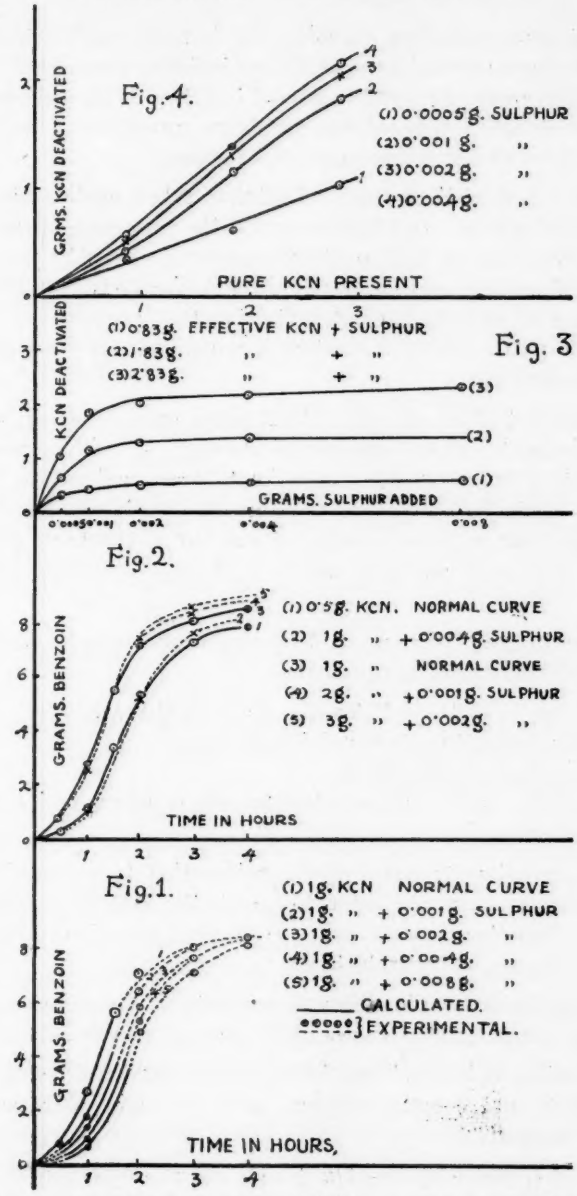
Fig.4.
GRMS. KCN DEACTIVATED
(1) 0·0005 g. SULPHUR
(2) 0·001 g. ,,
(3) 0·002 g. ,,
(4) 0·004 g. ,,
PURE KCN PRESENT
Fig. 3
KCN DEACTIVATED
(1) 0·83 g. EFFECTIVE KCN + SULPHUR
(2) 1·83 g. ,, + ,,
(3) 2·83 g. ,, + ,,
GRAMS. SULPHUR ADDED
Fig.2.
GRAMS. BENZOIN
(1) 0·5 g. KCN. NORMAL CURVE
(2) 1 g. ,, + 0·004 g. SULPHUR
(3) 1 g. ,, NORMAL CURVE
(4) 2 g. ,, + 0·001 g. SULPHUR
(5) 3 g. ,, + 0·002 g. ,,
TIME IN HOURS
Fig.1.
GRAMS. BENZOIN
(1) 1 g. KCN NORMAL CURVE
(2) 1 g. ,, + 0·001 g. SULPHUR
(3) 1 g. ,, + 0·002 g. ,,
(4) 1 g. ,, + 0·004 g. ,,
(5) 1 g. ,, + 0·008 g. ,,
CALCULATED.
EXPERIMENTAL.
TIME IN HOURS.

As shown in Part II each time-yield curve with the inhibitors can be replaced, in the earlier stages particularly, by a curve obtained with smaller

quantities of pure potassium cyanide. It is thus possible to find as described there, the amount of pure KCN functioning in presence of the inhibitor and hence the amount of cyanide rendered inactive. Fig. 2 shows that some of the curves obtained with sulphur and larger quantities of KCN, are coincident with those obtained from pure KCN alone.

Fig. 3 is a plot of the amount of sulphur taken against the amount of KCN rendered inactive. It will be seen that the curves are of the adsorption type, *i.e.*, the quantity of KCN rendered inactive rises rapidly to a maximum. The amount of sulphur required to saturate the cyanide is almost independent of the amount of cyanide present indicating that the amount adsorbed is very small, so that a constant solution remains with all quantities of KCN within the limits used.

Fig. 4 is a plot of the amount of KCN taken against the amount of KCN rendered inactive by given amounts of sulphur. It will be seen that the amount of KCN deactivated is approximately proportional to the amount taken. This again indicates that the amount of sulphur adsorbed is very small, so that with a given amount of sulphur a constant solution, not changed by the small amounts adsorbed by large amounts of cyanide, is obtained.

As shown in Part I (*loc. cit.*, p. 734) the reaction can be mathematically interpreted by the following equation :—

$$t - c' = -1/k_1[-5/n' + 3{\cdot}45 \log n' - 4{\cdot}60 \log (10 + X' - n')],$$

where n' = gm. benzaldehyde remaining at time t,

c' = constant of integration,

and $X' = 2k_2'/k_1$, k_2' being the heterogeneous constant and k_1 the homogeneous constant.

For the experiments now under consideration k_1 remained unchanged and was found to have the value $5{\cdot}7$; k_2', the velocity constant for the heterogeneous reaction, has the value $0{\cdot}185$ for 1 gm. of effective potassium cyanide per 10 gms. of benzaldehyde.

Hence we have for the different amounts of potassium cyanide and sulphur used, the calculated values of X′ shown in Table III.

The equations to be employed for (*a*) 1 gm. KCN and 0·001 g. sulphur, (*b*) 1 gm. KCN and 0·002 g. sulphur, and (*c*) 1 gm. KCN and 0·004 g. sulphur are respectively :—

$$(a) \quad -5{\cdot}7\,(t - 1{\cdot}24) = -5/n' + 3{\cdot}45 \log n' - 4{\cdot}60 \log (10{\cdot}028 - n')$$
$$(b) \quad -5{\cdot}7\,(t - 1{\cdot}36) = -5/n' + 3{\cdot}45 \log n' - 4{\cdot}60 \log (10{\cdot}022 - n')$$
$$(c) \quad -5{\cdot}7\,(t - 1{\cdot}60) = -5/n' + 3{\cdot}45 \log n' - 4{\cdot}60 \log (10{\cdot}0194 - n')$$

TABLE III.

KCN and Sulphur	Gram. KCN effective (δ)	$k_2' = 0 \cdot 185\delta$	$X' = 2k_2'/k_1 = 2k_2'/5 \cdot 7$
	(From time yield curves)		
1g. KCN & 0·001g. S	0·43	0·08	0·028
1g. KCN & 0·002g. S	0·34	0·063	0·022
1g. KCN & 0·004g. S	0·30	0·055	0·019

Equations for other quantities of potassium cyanide and sulphur were obtained in a similar manner.

The calculated values agree fairly well with the theoretical values up to about half the conversion of benzaldehyde, when benzoin begins to separate and the equation no longer applies. The application of these equations to calculate the course of the time reaction curves is shown in Fig. 1.

Other Inhibitors.

Carbon disulphide.—This was purified by repeated distillation and used in the form of a standard solution in benzaldehyde.

Thiobenzaldehyde.—This was prepared by Klinger's method.[2] Its action was investigated because it is formed when H_2S is passed into benzaldehyde, and it was found that a few bubbles of H_2S passed into benzaldehyde greatly inhibited the benzoin reaction.

Iodine.—Kahlbaum's resublimed iodine was employed and was found to give consistent results. It was used in the solid form as well as in the form of a standard solution in benzaldehyde.

Quinone.—Merck's quinone was steam-distilled and resublimed several times till it gave a constant melting point, 117·5° C. As with iodine, quinone was used both in the solid state as well as in the form of a standard solution in benzaldehyde. In performing experiments with minute quantities of quinone, a 0·00001% solution in benzaldehyde was prepared by the method of successive dilution.

Table IV summarises the results obtained at 100° C. by shaking 10 gms. benzaldehyde and 1, 2 and 3 gms. KCN with various amounts of the purified inhibitors.

[2] *Ber.*, 1876, **11**, 1895.

TABLE IV.

Time in hours	1 gm. KCN			2 gms. KCN			3 gms. KCN		
	Grams CS_2 added								
	0·05	0·1	0·2	0·05	0·1	0·2	0·05	0·1	0·2
1	2·09 g.	1·37 g.	0·80 g.	2·77 g.	2·10 g.	1·51 g.	3·15 g.	2·86 g.	2·50 g.
2	6·42 ,,	5·61 ,,	3·77 ,,	6·86 ,,	6·08 ,,	5·17 ,,	7·68 ,,	6·42 ,,	5·34 ,,
3	7·32 ,,	6·56 ,,	5·81 ,,	7·65 ,,	7·18 ,,	6·15 ,,	8·31 ,,	7·81 ,,	6·46 ,,
4	7·49 ,,	6·14 ,,	6·14 ,,	—	—	—	—	—	—
	Grams C_6H_5CHS added								
	0·01	0·02	0·04	0·01	0·02	0·04	0·01	0·02	0·04
1	2·23 g.	1·70 g.	1·01 g.	3·09 g.	2·55 g.	1·48 g.	3·50 g.	3·00 g.	2·22 g.
2	6·78 ,,	6·36 ,,	5·09 ,,	7·10 ,,	6·87 ,,	6·18 ,,	7·65 ,,	7·25 ,,	6·71 ,,
3	8·01 ,,	7·88 ,,	7·51 ,,	8·39 ,,	8·23 ,,	8·06 ,,	8·62 ,,	8·35 ,,	8·15 ,,
	Grams Iodine added								
	0.00002	0·0002	0·002	0·00002	0·0002	0·002	0·00002	0·0002	0·002
1	2·34 g.	2·20 g.	1·80 g.	3·31 g.	2·98 g.	2·58 g.	3·70 g.	3·37 g.	2·97 g.
2	6·83 ,,	6·65 ,,	6·40 ,,	7·44 ,,	7·30 ,,	6·93 ,,	7·48 ,,	7·20 ,,	7·01 ,,
3	8·14 ,,	8·03 ,,	7·90 ,,	8·49 ,,	8·43 ,,	8·04 ,,	8·48 ,,	8·45 ,,	8·33 ,,
	Grams Quinone added								
	0·00004	0·0002	0·0005	0·0002	0·0005	0·001	0·0002	0·0005	0·001
1	2·10 g.	0·79 g.	0·52 g.	2·20 g.	1·90 g.	1·84 g.	2·94 g.	2·49 g.	2·42 g.
2	6·95 ,,	6·70 ,,	5·91 ,,	7·33 ,,	7·02 ,,	6·36 ,,	7·72 ,,	7·57 ,,	7·42 ,,
3	8·10 ,,	8·11 ,,	7·84 ,,	8·51 ,,	8·40 ,,	8·32 ,,	8·73 ,,	8·61 ,,	8·54 ,,

A comparison of the results with the inhibitors examined indicates that if they are arranged according to their inhibitory power, they stand in the

following order :—quinone, iodine, sulphur, thiobenzaldehyde and carbon disulphide. It would appear that the marked inhibitory action shown by H_2S is not due to the formation of thiobenzaldehyde only.

Table V shows the least quantity of the inhibitors used required to show inhibition with 10 gms. benzaldehyde, and 1 gm. KCN for 1 hour at 100° C. The amount of inhibitor required to saturate 0·83 gm. effective KCN is also shown.

TABLE V.

Inhibitor	Minimum quantity used	Yield obtained in 1 hour with 1 gm. KCN, normal yield being 2·72 gms.	Minimum quantity required nearly to saturate the surface of the cyanide	Minimum proportion showing inhibition in parts of benzaldehyde
Quinone ..	0·00001 gm.	2·36 gms.	0·0005 gms.	1 : 10^6
Iodine ..	0·00002 ,,	2·34 ,,	0·002 ,,	1 : 500,000
Sulphur ..	0·0005 ,,	1·98 ,,	0·001 ,,	1 : 20,000
Thiobenzaldehyde	0·01 ,,	2·23 ,,	0·04 ,,	1 : 1,000
Carbon disulphide	0·05 ,,	2·09 ,,	0·1 ,,	1 : 200

The results obtained with these inhibitors are of the same type as those obtained with sulphur, *viz.*, the autocatalytic portion of the resulting curves have a constant slope practically independent of the amount of cyanide or sulphur. Figs. 5, 6, 7 and 8 are a plot of the amount of inhibitors taken against the amount of potassium cyanide deactivated by them. The curves are all of the adsorption type ; only small fractions of the amount dissolved appears to be adsorbed, since the amount of potassium cyanide rendered inactive is roughly proportional to the amount of cyanide present. The results with quinone are particularly interesting, for by using 0·3 gm. of pure potassium cyanide, it was established as a result of large number of repeated experiments, that the normal yield of 1·8 gm. obtained from 10 gms. of benzaldehyde for 2 hours was reduced to 1·3 gm. when benzaldehyde containing quinone in the proportion of 1 part in ten million was employed.[3]

Adsorption Experiments in Presence of Inhibitors.

According to the theory outlined in Part II (p. 905) and confirmed by the present experiments, the inhibition of the benzoin reaction is assumed to be due to the adsorption of the inhibitor by the solid cyanide. From this it follows that if benzaldehyde containing an inhibitor is allowed to

[3] See *Curr. Sci.*, 1935, **4**, 94.

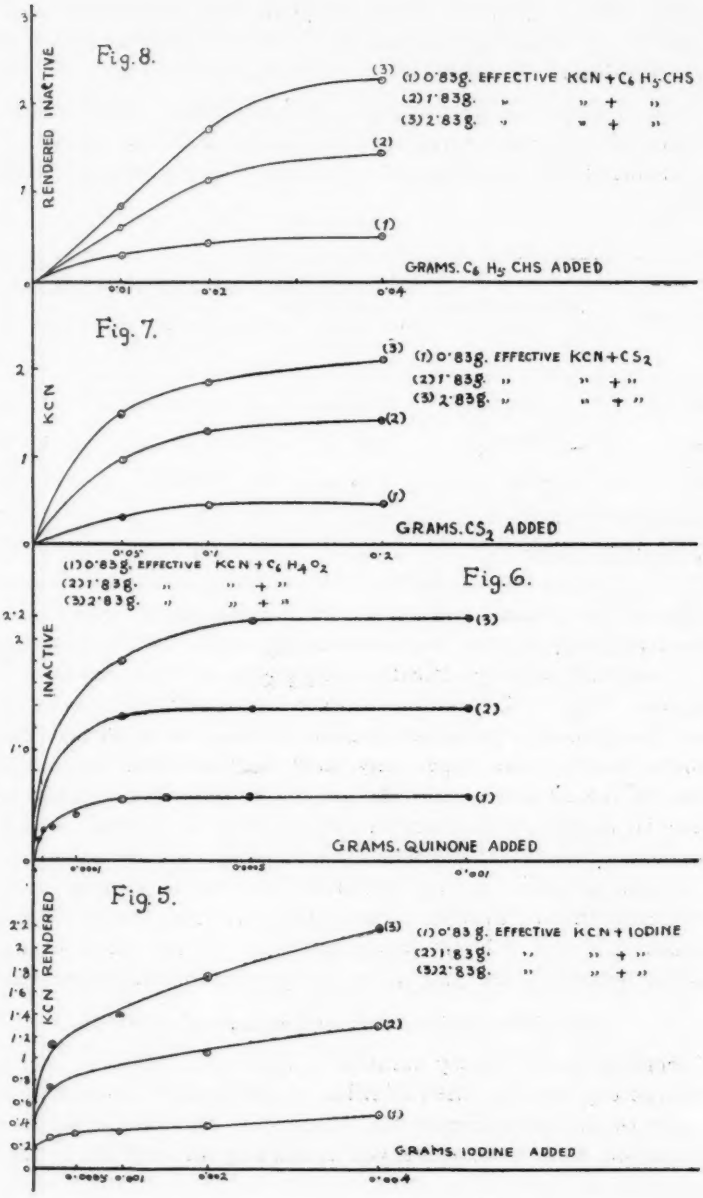
Fig. 8.
RENDERED INACTIVE
(1) 0·83g. EFFECTIVE KCN + C_6H_5CHS
(2) 1·83g. " " + "
(3) 2·83g. " " + "
GRAMS. C_6H_5CHS ADDED
Fig. 7.
KCN
(1) 0·83g. EFFECTIVE KCN + CS_2
(2) 1·83g. " " + "
(3) 2·83g. " " + "
GRAMS. CS_2 ADDED
Fig. 6.
(1) 0·83g. EFFECTIVE KCN + $C_6H_4O_2$
(2) 1·83g. " " + "
(3) 2·83g. " " + "
INACTIVE
GRAMS. QUINONE ADDED
Fig. 5.
KCN RENDERED
(1) 0·83 g. EFFECTIVE KCN + IODINE
(2) 1·83g. " " + "
(3) 2·83g. " " + "
GRAMS. IODINE ADDED

stand at room temperature in contact with quantities of KCN too small to produce benzoin (less than 0·17 g.)[4] the inhibitor should be adsorbed, and the benzaldehyde when filtered from the potassium cyanide in an atmosphere of nitrogen should show an improved yield of benzoin. Table VI shows that these predictions are correct.

TABLE VI.

Standard Yields: 1 *hour*, 2·72 *gms.*; 2 *hours*, 7·1 *gms.*

Inhibitor	Amount added in gms.	Time in hours	Normal yield in presence of inhibitor (gms.)	Yield after filtration (gms.)
Quinone ..	0·0002	1	0·79	1·47
,, ..	,,	2	6·70	7·20
Iodine ..	0·002	1	1·80	2·74
,, ..	,,	2	6·40	6·99
Sulphur ..	0·001	1	1·79	2·79
,, ..	,,	2	6·52	7·15
Thiobenzaldehyde ..	0·01	1	2·23	2·69
,, ..	,,	2	6·78	6·91
Carbon disulphide ..	0·2	1	0·80	1·64
,, ..	,,	2	3·77	4·94
Quinol* ..	0·05	1	2·01	0·14
Potassium iodide* ..	0·05	1	0·30	1·38
,, ..	,,	2	2·18	5·39
Potassium chloride* ..	0·4	1	2·25	2·84
,, ..	,,	2	6·51	6·98
Sodium chloride* ..	0·4	1	2·18	2·76
,, ..	,,	2	6·50	7·03

It was confirmed by experiment that no benzoin was formed at ordinary temperatures during the period of adsorption.

It will be noted that the only inhibitor of which the effect is not decreased by standing in presence of pure KCN is quinol. Thinking that the increased

[4] See Part I, *loc. cit.*, p. 730.

* Examined in Part II.

inhibition might be due to its conversion to quinone we examined the effect of the latter with the results given above.

These experiments provide the basis of a method for purifying benzaldehyde so as to make it suitable for use in the investigation of this reaction. Various commercial specimens of benzaldehyde (50 gms.) were allowed to stand overnight in contact with 0·1 gm. KCN. It was found that by this treatment the yield of benzoin under standard conditions was improved, and the normal yield was usually obtained. Complete purification was not obtained if more than 50 gms. of benzaldehyde was taken at a time with 0·1 gm. of pure potassium cyanide.

Summary.

(1) It is shown that sulphur, carbon disulphide, thiobenzaldehyde, iodine and quinone act as inhibitors in the heterogeneous reaction between solid potassium cyanide and pure benzaldehyde.

(2) The action is due to the adsorption of the inhibitor on the surface of the solid potassium cyanide.

(3) Inhibition can be detected with benzaldehyde containing one part in ten million of quinone.

(4) Crude benzaldehyde can be purified for use in the benzoin reaction by keeping it at room temperature in 50 gm.-lots in an atmosphere of nitrogen in contact with 0·1 gm. of potassium cyanide.

THE RAMAN SPECTRA OF SOME FORMATES AND THE CONSTITUTION OF FORMIC ACID.

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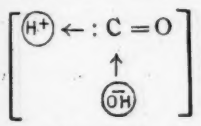
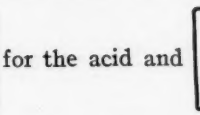
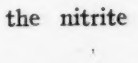
1. Introduction.

The most interesting among the fatty acids is formic acid on account of the striking differences between its chemical properties and those of its higher homologues. The most important among its exceptional properties is that it is about twelve to twenty times stronger as an acid than acetic or propionic acids; it is, unlike the latter, easily oxidisable and does not form a chloride or an anhydride corresponding to acetyl chloride or anhydride. Some of these properties have been explained on the basis of the older hypothesis that an aldehyde group COH, is present in the molecule. In a recent note to *Nature*[1] Sir P. C. Ray has put forward the suggestion, based on the experimental work of P. B. Sarkar, that the anomalous behaviour of formic acid is due to a difference in its chemical constitution, namely, that "*the ionisable hydrogen in it is not the hydrogen of the hydroxyl group, as in the case of the other fatty acids but the hydrogen attached to the carbon atom*". The electronic conception based on this assumption is given by him as

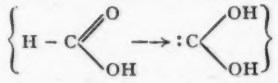
 for the acid and  for the formate ion. He establishes the identity of the former with the well-known electronic configuration of the nitrite ion  and finds support for it in the possibility of preparing mixed crystals of formates and nitrites of a few metals.

Exception to this suggestion has, however, been taken by T. R. Seshadri[2] who has pointed out that it is wholly unjustifiable from other important

[1] Ray, P. C., *Nature*, 1934, **133**, 646.

[2] Seshadri, T. R., *Current Science*, 1935, **3**, 383.

chemical considerations. This author has explained the classical synthesis of formates, the reducing power of the formate ion and other exceptional properties on the assumption "*that the carboxyl group in the acid is linked to a hydrogen atom (aldehyde group) whereas in its homologues the carboxyl is linked to the alkyl groups and in the course of certain reactions formic acid is capable of undergoing isomeric change to dihydroxymethylene.*"



Thus according to the suggestions of Sir P. C. Ray, the formate ion does not contain the CH group, whereas Seshadri presumes that it is present in it, just as in the case of acetates, etc. This issue is capable of being decided by the method of the Raman effect where the presence of the CH group in the metallic formates could be detected directly by experiment. At the suggestion of Dr. Seshadri, the author has investigated this problem and the present paper deals with the results obtained with the formates of sodium, calcium, cadmium and lead both as crystals and aqueous solutions. The measurements give indication of the existence of the CH group in the compounds studied.

2. *Experimental Technique and Results.*

The experimental arrangement was essentially the same as that described by the author in the previous communications.[3] Extra-pure crystals of sodium, calcium and cadmium formates were prepared and kindly lent to the author by Dr. Seshadri of the Andhra University, Waltair. Lead formate crystals were the extra-pure variety supplied by Kahlbaum. Since sodium formate is hygroscopic it was kept sealed in an evacuated tube during exposure. Cadmium formate was cooled during exposure by water circulation in order to avoid the loss of water of crystallisation. Using specially backed Ilford "golden isozenith" plates H. and D. 1400, the time of exposure was about twelve hours for the crystal powders and twenty-four hours for the aqueous solutions. The plates were measured on a Hilger comparator, alongside of an iron-arc spectrum and the results are set out in Table I. The Raman lines due to CH are indicated in the enlarged photograph of the spectra of 42% aqueous solution of sodium formate and of the crystals of lead formate which are reproduced in the accompanying Plate. In order to provide a comparison, the spectrum of formic acid* enlarged to the same scale, has also been reproduced.

[3] Venkateswaran, C. S., *Proc. Ind. Acad. Sci.*, A, 1935, 1, 850; 2, 119.

* The author's thanks are due to Mr. R. Ananthakrishnan for his kind permission to reproduce his formic acid spectrum here for reference.

TABLE I.

Substance	Raman lines in cm.$^{-1}$								Remarks
Sodium formate crystals ..	..	2834 (w,dif)	..	1717 (v.w)	1555 (v.w)	1397 (v.w)	1365 (m,sh)	..	
Sodium formate solution 42%	..	2834 (m,dif)	2734 (w,dif)	..	..	..	1353 (v.st,sh)	857 (w)	St. water band.
Calcium formate crystals ..	2973 (v.w)	2849 (w,dif)	..	1716 (w)	1550 (w)	1397 (m,dif)	1359 (w)	..	
Calcium formate solution 15%	..	2834 (m,dif)	2721 (w,dif)	..	..	..	1353 (st,sh)	..	
Cadmium formate crystals ..	..	2849 (w,dif)	..	1716 (w)	1550 (v.w)	1397 (w)	1359 (m,dif)	..	
Cadmium formate solution 3%	..	..	..	..	..	..	1353 (w)	..	
Lead formate crystals ..	2976 (w)	2847 (w,dif)	..	1717 (m)	1534 (m)	1397 (w)	1347 (v.st)	..	Line at 200 (doubtful)

The abbreviations in this and the following Table mean: v.st=very strong, st=strong m=medium intensity, w=weak, v.w=very weak, and dif=diffuse.

3. *Discussion of Results.*

Although the Raman spectra of formic acid[4] and some of its esters[5] have been studied by earlier investigators, the presence of the CH group in the formate ion can be established only from the Raman spectra of the metallic formates where the same group is not present in any other form. In Table II, the frequency shifts of formic acid and methyl formates are given along with the results obtained by the author for the metallic formates. Similar data are also given from Dr. Krishnamurti's work for acetic acid and sodium acetate. In general the metallic salts either in the solid state or as aqueous solutions, yield fewer lines than the acids. Among the four compounds studied (Table I) in the solid state, lead formate has given the most intense picture in spite of the fact that the other formates, especially the cadmium salt, were available in the form of better crystals. Similar observations with the acetates have also been made by Krishnamurti.[6] Sodium formate

[4] Ganesan, A. S., and Venkateswaran, S., *Ind. Jour. Phys.*, 1929, **4**, 195.
Dadieu and Kohlrausch, *Physikal Z.*, 1929, **30**, 384.
Parthasarathy, S., *Ind. Jour. Phys.*, 1931, **6**, 287.
Kohlrausch, K. W. F., Koppl, F., and Pongratz, A., *Z. f. Phys. Chem.*, B, 1933, **21**, 242.

[5] Kohlrausch, K. W. F., and Pongratz, A., *Z. f. Phys. Chem.*, B, 1933, **22**, 373.

[6] Krishnamurti, P., *Ind. Jour. Phys.*, 1931, **6**, 309.

TABLE II.

Formic acid	Methyl formate	Lead formate crystals	Sodium formate solution	Acetic acid (Incomplete)	Sodium acetate
189±80 (5)	334 (3b)	200 (?)		440 (3)	
673 (3b)	762 (2)			614 (5)	647 (1)
859 (½)	912 (10)		857 (1)	889 (6)	925 (4)
1050 (1b)	1030 (½)				
1200 (2)	1157 (1b)			1280 (1b)	
	1247 (½b)				
		1347 (5)	1353 (8)		1346 (3)
1398 (5)	1378 (3b)	1397 (1)		1368 (4b)	
	1445 (2v.b)			1432 (4b)	1411 (1b)
1672 (4)		1534 (2)			
1724 (2)	1717±6 (5v.b)	1717 (1)		1669 (4b)	1647 (1)
	2839 (3)	2847 (1)	2732 (2) 2834 (5)		
2963 (7b)	2955 (3)	2976 (½)		2940 (10b)	2934 (5b)
	3030 (2v.b)				

is the most soluble of the salts studied and a 40% solution of it has yielded a very intense spectrum. As can be seen from the accompanying Plate, the most prominent line in the crystal is the one at 1347 and it is followed by a faint companion at 1397 in the formates of sodium, cadmium and lead. In the case of calcium formate, the line at 1397 is stronger than the one at 1359. The corresponding line in formic acid falls at 1398. Parthasarathy[7] has observed that it is followed by a wing to the violet side and as can be seen from the Plate the centre of this wing approximately coincides with the frequency shift 1347. If we assume that 1398 is the frequency in the unionised state, it follows that in the crystals of metallic formates there is a small percentage of the solid possessing covalent linkage giving rise to this line. In the calcium salt this percentage is considerably higher than in the

[7] Parthasarathy, S., *Loc. cit.*

others. The line at 1347 is evidently characteristic of the ionised group HCO, and shifts to a higher frequency as we pass from lead to sodium. The wing to the violet side in the acid is also to be attributed to a small percentage of dissociation in it. This line is also shifted to a slightly higher frequency in the aqueous solutions and is the strongest line in all cases. This line is attributed by Kohlrausch and his co-worker[8] to the deformation oscillation of the CH in the aldehyde group HCO.

The valence frequency due to the CH binding appears in formic acid as a broad line at 2963 and as three lines at 2839, 2955 and 3030 in methyl formate. In the crystalline formates of lead and calcium two diffuse lines are clearly present at 2847 and 2986 but in the aqueous solution of the sodium and calcium salts they are replaced by two broad lines at 2834 and 2732. The possibility that these lines are excited by the 4358 radiations of the source is excluded on the consideration that the corresponding lines that would be excited by 4047 in such a case, do not appear in the region between 4358 and 4047. (See Sodium formate picture.) Thus, in the ionised state the line due to CH in the formates suffers a large shift of more than 130 wavenumbers towards lower frequency and coincides with the frequency shift of 2839 in methyl formate. In the case of acetates this change is considerably less. *These two lines, namely,* 2834 *representing the valence oscillation and* 1347 *representing the deformation oscillation of the HCO group, indicate beyond doubt the presence of this group in the formate ion.*

Another important feature of the spectra of the formates of which special mention may be made, is the presence of the line at 1534 which appears clearly in the spectrum of lead formate. This line is present very feebly in the other crystals also. But in the aqueous solutions, its presence could not be detected, for the water band excited by the 4046 radiations happens to fall in the region where it would appear. It may be inferred from Table II that no such line is present in formic acid or its esters or in acetic acid and acetates. This frequency is also too low to be attributed to the carboxyl group C = O and its origin is difficult to understand at this stage. But it is possible that it is in some way connected with the change of formic acid to the form dihydroxymethylene as suggested by Seshadri.

It is surprising that the frequency due to C = O appears only very weakly at 1717 in the spectra of the crystals. Due to a large number of feeble mercury lines in that region it could be identified only with great difficulty. In the spectra of the aqueous solutions this line, if present, would be superposed on the water band and hence could not be observed. Similar

[8] Kohlrausch, K. W. F., and Koppl, F., *Z. f. Phys. Chem.*, 1934, **24**, 370.

weakening of the carboxyl frequency has been previously noticed by Ghosh and Kar[9] and Krishnamurti[10] in metallic acetates and as is pointed out by the former authors, wherever C = O group forms part of the negative ion, it is considerably weakened. The weak line at 857 in the water solution of sodium formate is to be compared to the line at 859 in formic acid.

The influence of formates on the water bands is negligible. The well-defined minima separating the three bands in pure water are not clear in the solutions of formates and a slight narrowing of the bands is also observed.

In conclusion the author wishes to express his heartfelt thanks to Prof. Sir C. V. Raman for his interest in the work. The investigation was undertaken at the suggestion of Dr. Seshadri of the Andhra University, Waltair, to whom the author's best thanks are due.

Summary.

The Raman spectra of the formates of sodium, calcium, cadmium and lead have been investigated both as solid and as aqueous solutions and the following average frequencies have been obtained for the formate ion :— 2834, 2734, 1717, 1534, 1347 and 857 cm.$^{-1}$ The presence of the lines at 2834 and 2732 gives direct experimental evidence of the existence of CH group in formic acid. The solids have yielded faint lines also at 2976 and 1398. The frequencies are compared with those of formic acid and its esters and acetic acid and acetates. The presence of the line at 1534 seems to be characteristic of the formates.

[9] Ghosh and Kar, *Jour. Phys. Chem.*, 1931, **35**, 1735.

[10] Krishnamurti, P., *Loc. cit.*

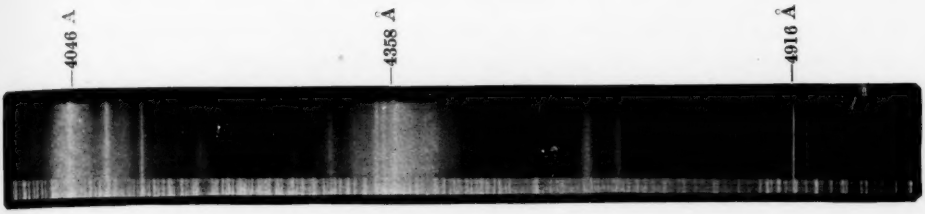


FIG. 1. Formic acid (liquid).

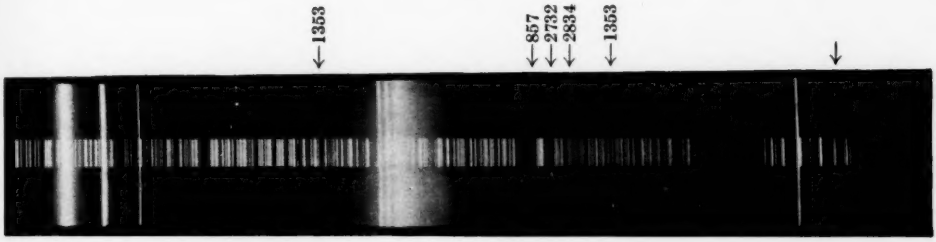


FIG. 2. Sodium formate (aq. soln.).

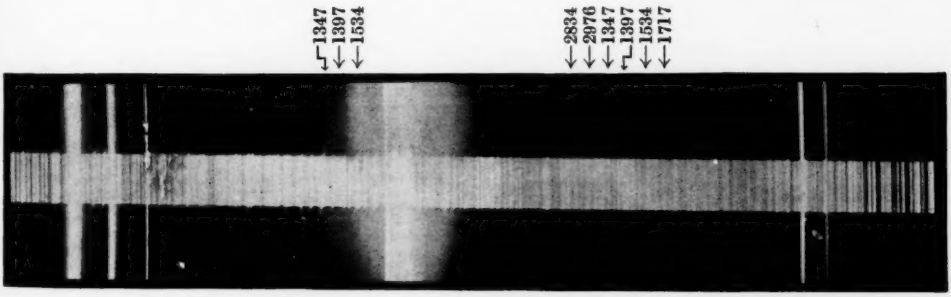


FIG. 3. Lead formate (crystals).

Raman Spectra.

MAGNETIC ANISOTROPY OF NATURALLY OCCURRING SUBSTANCES.

I. Mother of Pearl.

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(From the Department of Physics, Indian Institute of Science, Bangalore.)

Received November 11, 1935.
(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

1. *Introduction.*

The recent investigations of K. S. Krishnan and his collaborators[1] have shown that in magne-crystallic action we have a powerful method of determining molecular orientations in crystals. When magnetically anisotropic molecules or ions are arranged regularly as they are in a crystal, the crystal also will show anisotropy, the magnitude of which will depend upon the orientation of the molecules in the crystal lattice. A correlation of the anisotropy of the crystal with that of the individual molecules enables the orientations of the latter to be calculated. The approximate molecular orientations in the naphthalene crystal were first determined by S. Bhagavantam[2] by this method. Recently, accurate determinations of anisotropy for a large number of para- and dia-magnetic crystals, both organic and inorganic, have been made by Krishnan and his collaborators, and in some favourable cases such as biphenyl and dibenzyl, the orientations of the molecules have been determined with precision.

Just as a crystal is an aggregate of ions or molecules regularly arranged, there are naturally occurring substances which are known to be aggregates of minute crystals in a more or less regular arrangement. If the individual crystals are anisotropic, we should expect the substance also to show anisotropy, and we can employ Krishnan's method for determining the crystal orientations. One such substance is the nacre of iridescent shells. The magnetic properties of nacre have not been investigated quantitatively, although Nacken[3] and others[4] have observed its anisotropy in connection with the study of the differences between real and "culture" pearls. The latter contain a small spherical inner core of mother-of-pearl and as a consequence take up a definite orientation in a magnetic field unlike real pearls, which do not show any preferred orientation. The object of the present investigation is chiefly to determine the anisotropy of nacre quantitatively with a view to

gain some knowledge of its structure and thereby supplement what is already known from X-ray and optical studies.

2. *Structure of Nacre.*

It is well known that mother-of-pearl consists of minute crystals of aragonite arranged in thin layers and honey-combed in between an organic cementing medium called conchyolin.[5] Aragonite is diamagnetic, and its magnetic properties are known both as regards its absolute susceptibilities along the three axes (Voigt and Kinoshita)[6] and magnetic anisotropy (Krishnan)[7].

By examination under the polarising microscope, W. J. Schmidt[8] has shown that the aragonite crystals are orientated in nacre with the *c*-axes normal to the elementary laminæ. Recently, from a study of the diffusion haloes of nacre, Sir C. V. Raman[9] has drawn attention to the structural differences in the shells of the three main classes of molluscs. These differences have been verified by Dr. S. Ramaswamy[10] by X-ray analysis. He has found that while the *c*-axes of the crystals are orientated normal to the laminæ in all the shells, the orientations of the *a* and *b* axes are different in the various shells, *viz.*, a random orientation in *Turbo* and *Trochus* and a preferred orientation in *Margaratifera vulgaris* and *Mytilus viridis*. Evidence of twinning has been found in *Nautilus pompilius*, the twins being arranged symmetrically with respect to the lines of growth. In a more recent paper[11] a preferred orientation has been found by the same author in the case of *Haliotis* also with however a very large error in orientation.

3. *Determination of the Anisotropy of Nacre.*

This was done by means of the method of oscillations developed by Krishnan.[12] If χ_1 and χ_2 are algebraically the maximum and minimum values of the susceptibility along two perpendicular directions in the plane of oscillation of a body suspended by means of a quartz fibre in a uniform magnetic field, it will orientate itself with the χ_1 axis in the field direction. If the torsion head is turned so that the torsion of the fibre is zero at this position, and if T_1 and T are the periods of oscillation in and outside the field respectively, we have,

$$\chi_1 - \chi_2 = \frac{1}{m} \cdot \frac{c}{H^2} \cdot \frac{T^2 - T_1^2}{T_1^2}$$

$\chi_1 - \chi_2$ = Specific anisotropy in the plane of oscillation.

c = Modulus of torsion of the fibre.

m = Mass of the body.

H = Field strength in Gauss.

Some preliminary experiments showed that all the shells examined are diamagnetic, the direction of maximum diamagnetic susceptibility being normal to the plane of the laminæ. This direction then is one of the principal magnetic axes in nacre. The other two axes lie in the laminar plane and could be easily located by observing the orientation in the field.

The following precautions were taken :—

(1) The specimens selected were seen to be as white as possible and free from discolourations. By chemical test it was found that none of the pieces contained even traces of iron.

(2) The pieces of nacre were carefully cleaned before use.

(3) The elementary laminæ are usually inclined at a small angle to the shell surface. The shell faces were ground until they were parallel to the laminæ in the pieces used.

Experimental Details.—Fine quartz fibres drawn in the flame were employed. The pieces were mounted on the suspension as described in Krishnan's paper.

The field was tested for homogeneity and the strength determined by means of the Ballistic Galvanometer, in the usual way. Some preliminary experiments were made with a single crystal of calcite for which the anisotropy values are known, with satisfactory results.

The modulus of torsion c of the fibre was determined by observing the period of oscillation of a small rectangular plate of glass suspended at its end of which the moment of inertia about the axis of suspension can be calculated from the dimensions.

The arrangement shown in Fig. 1 was employed for observing the orientation of the shell in the field.

The piece of shell is illuminated from below by means of a powerful lamp and condensing lens. The image reflected at the glass plate G kept inclined at an angle of 45° is viewed through the short focus telescope T. The telescope is provided with a circular brass scale by means of which its angular rotations can be measured. The orientations of the shell can be easily determined by rotating the telescope suitably such that the cross-fibre coincides with any position of the image of the shell.

The angle of inclination of the elementary laminæ to the shell surface can be determined magnetically, since the orientation of the laminar plane is found to be always along the field in the case of all the shells. This angle has also been measured optically by Sir C. V. Raman.[13] The values of the angle found by the optical and the magnetic methods agreed satisfactorily.

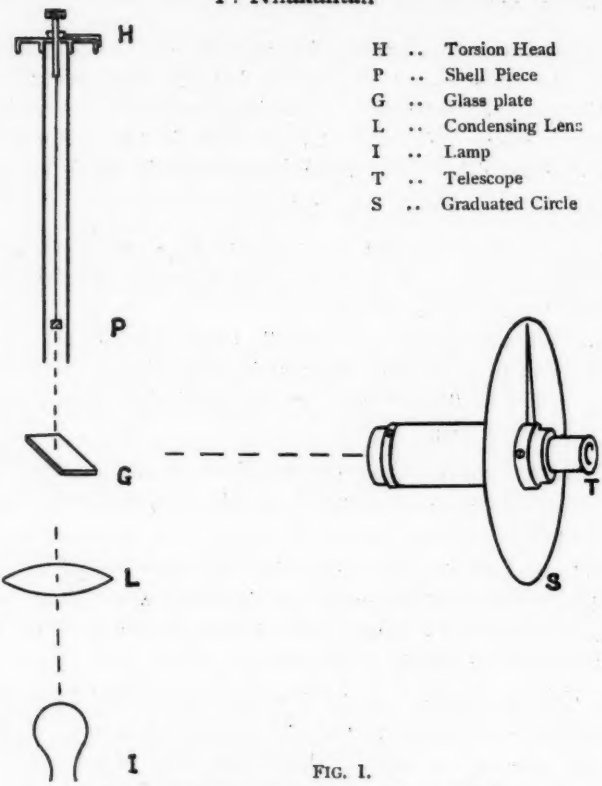

FIG. 1.

4. Measurement of Absolute Susceptibility.

This was done by Rabi's[14] null method, the liquid used being a saturated solution of potassium iodide. The piece of shell was suspended by means of a torsionless silk fibre about 60 cms. long, with one of its magnetic axes vertical. It orientated itself in the field with the axis of maximum diamagnetic susceptibility normal to the field. The measurements give the susceptibility along that axis which is parallel to the field.

The concentration of the potassium iodide solution was determined by titration against a standard solution of silver nitrate using eosin as indicator. From the measured values of the concentration used, the density of the solution, and the density of the shell, we can deduce the susceptibility of the shell making use of well-known relations.

5. Results.

The shells investigated were *M. margaratifera, Turbo, Haliotis, Mytilus viridis* and *Nautilus pompilius*. Table I gives the observed values of the anisotropy. Krishnan's values for aragonite are also included for comparison.

TABLE I.

Unit: 10^{-6} *of a C.G.S. Electromagnetic Unit.* $\chi_1' > \chi_2' > \chi_3'$ *algebraically.*

Class	Shell	Mode of Suspension	Orientation	Specific Anisotropy		Remarks
				Observed	Calculated	
Gastropod	*Turbo* sp.	(A) Laminar plane horizontal	..	$\chi_1'-\chi_2'=0{,}05$	0,07	Orientation in the laminar plane, indefinite
		(B) Plane vertical and χ'_1 axis vertical	Plane parallel to the field	$\chi_2'-\chi_3'=5{,}6_0$		
		(C) Plane vertical and χ'_2 axis vertical	,,	$\chi_1'-\chi_3'=5{,}6_7$		
,,	*Haliotis* sp.	(A)	..	$\chi_1'-\chi_2'=0{,}07$	0,1	
		(B)	Plane parallel to the field	$\chi_2'-\chi_3'=6{,}0$		
		(C)	,,	$\chi_1'-\chi_3'=6{,}1$		
Bivalve	*M. Margaratifera*	(A)	Line of growth nearly perpendicular to the field	$\chi_1'-\chi_2'=0{,}21$	0,1	
		(B)	Plane parallel to the field	$\chi_2'-\chi_3'=5{,}6$		
		(C)	,,	$\chi_1'-\chi_3'=5{,}7$		
Bivalve	*Mytilus viridis*	(A)	Line of growth nearly perpendicular to the field	$\chi_1'-\chi_2'=0{,}16$	0,1	
		(B)	Plane parallel to the field	$\chi_2'-\chi_3'=5{,}7$		
		(C)	,,	$\chi_1'-\chi_3'=5{,}8$		
Cephalopod	*Nautilus pompilius*	(A)	Line of growth nearly perpendicular to the field	$\chi_1'-\chi_2'=0{,}5$	0,3	Comparatively large anisotropy in the laminar plane
		(B)	Plane parallel to the field	$\chi_2'-\chi_3'=6{,}1$		
		(C)	,,	$\chi_1'-\chi_3'=6{,}4$		

TABLE II.

Anisotropy of Aragonite (Krishnan).

Unit: 10^{-8} *of a C.G.S. Electromagnetic Unit.*

Mode of Suspension	Orientation	Specific Anisotropy
a-axis vertical	*b*-axis along the field	4·2 $\chi_b - \chi_c = 4 \cdot 2$
b ,, ,,	*a* ,, ,,	4·0 $\chi_a - \chi_c = 4 \cdot 0$
c ,, ,,	*b* ,, ,,	0·13

TABLE III.

Absolute Susceptibility of the Shells.

Shell	Susceptibility in a direction normal to the laminar plane
Turbo	$-0{,}39\ 10^{-6}$
Haliotis	0,38 ,,
M. margaratifera	0,39 ,,
Mytilus viridis	0,39 ,,
Nautilus pompilius	0,36 ,,

TABLE IV.

Density of the Shells.

Shell	D in Gm/cm^3
Turbo	2,77
Haliotis	2,73
M. margaratifera	2,78
Mytilus viridis	2,80
Nautilus pompilius	2,62

Density of Aragonite .. 2·92

For the sake of brevity, the magnetic axes are denoted as the χ_1', χ_2' and χ_3' axes. The χ_3' axis is normal to the elementary laminæ. $\chi_1' - \chi_2'$, $\chi_2' - \chi_3'$ and $\chi_1' - \chi_3'$ are respectively the anisotropies in the respective planes. If two of these are determined, the third can also be easily obtained from these. As a check, the third was also independently determined.

The values of anisotropy differed by about 10% for the pieces taken from different parts of the same shell. The stated values represent only an average.

It will be seen that the anisotropies of the shells corresponding to the modes of suspension B and C are higher than should be expected from aragonite alone. This suggested that the conchyolin itself might have an anisotropy which adds itself to that of the aragonite crystals. An attempt was made to observe this anisotropy directly, by isolating the conchyolin. The aragonite was carefully dissolved off by dilute hydrochloric acid. The gas evolved had to be squeezed out from time to time since its accumulation prevented further action. This, however, could not be done without disturbing the conchyolin layers. One could not be sure, therefore, whether conchyolin retained its structure after its separation. This element of uncertainty, which is unavoidable, is a serious drawback of the method.

It was a matter of difficulty to prepare the conchyolin from *Nautilus pompilius* since it easily broke up and lost its structure. *Haliotis*, however, gave more satisfactory specimens.

The results obtained were inconclusive, for whereas two specimens showed slight anisotropy, others were only feebly so.

Conchyolin was found to be diamagnetic.

6. *Discussion.*

The anisotropy of nacre definitely indicates that the *c*-axes of aragonite crystals are orientated normal to the elementary laminæ in the case of all the shells. This is in accord with the results of X-ray and optical investigations.

The high values of the anisotropy for the (B) and (C) modes of suspension show that there is an additional anisotropy over and above that due to the aragonite crystals. The only way of explaining this seems to be to attribute anisotropy to conchyolin itself, although no conclusive results could be obtained by direct experiments on the separated conchyolin, owing to experimental uncertainties. If we assume that conchyolin is anisotropic, we at once arrive at two significant conclusions; firstly, that the molecules are anisotropic themselves, and secondly, that they are arranged more or less regularly in a quasi-crystalline structure. Conchyolin belongs to the class of sklero-proteins

and its empirical formula is $C_{30}H_{48}N_9O_{11}$. The structural formula is not known. The indirectly observed rather considerable anisotropy would indicate the presence of aromatic groups in the molecule, these being arranged with their planes parallel to the laminar planes.

It is difficult to draw definite conclusions as regards the orientations of the *a* and *b* axes of the aragonite crystals on account of the fact that the *c*-axis is one of approximate magnetic symmetry and that there are a few complications such as :—

(1) Slight differences in the curvatures of the elementary laminæ in different directions. The error caused by this was eliminated as far as possible by choosing very small pieces for experiment.

(2) The difficulty in mounting the piece with the laminar plane exactly horizontal. A spurious anisotropy of a small order can be caused by this.

(3) Natural irregularities in the elementary laminæ such as small pits and elevations.

We can however tentatively arrive at the following conclusions :—

In *Turbo* and *Haliotis*, the *a* and *b* axes are oriented more or less at random, since the anisotropy is very small in the laminar plane. This is in general agreement with the X-ray analysis by Dr. Ramaswamy. The preferred orientation of the *a* and *b* axes which he has found for *Haliotis* cannot, however, be detected by the magnetic method, since, owing to the very large error in orientation reported, the anisotropy will be negligibly small.

In *M. margaratifera* and *Mytilus viridis*, a preferred orientation is probably present, with the *a*-axis approximately along the line of growth. In the case of *Nautilus pompilius*, however, the anisotropy is comparatively large. Two explanations are possible ; it is either due to the conchyolin which is present in comparatively large quantity, or to a preferred tilting of the *c*-axes of the aragonite crystals in the direction of the line of growth, in the specimens examined.

The absolute diamagnetic susceptibility of the shells appears to be lower than that of aragonite in all cases, *Nautilus pompilius* having the lowest value.

The present investigation shows that the determination of the magnetic anisotropy of many natural substances is likely to throw some light on their constitution and structure. Further work in this direction is being undertaken.

In conclusion, I thank Sir C. V. Raman, Kt., F.R.S., N.L., who suggested the problem and under whose guidance the work was carried out.

Summary.

The magnetic anisotropies of the nacre of *Turbo*, *Haliotis*, *M. margaratifera*, *Mytilus viridis* and *Nautilus pompilius*, respectively, have been determined. The observations indicated that the *c*-axes of the aragonite crystals are in every case normal to the elementary laminæ. A random orientation of the *a* and *b* axes in *Turbo* and *Haliotis*, and a preferred orientation, with the *a*-axes approximately along the line of growth for *M. margaratifera* and *Mytilus viridis*, are tentatively suggested. A quasi-crystalline structure for conchyolin is suspected. The absolute susceptibilities of the shells have also been determined.

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REFRACTIVE INDICES AND DISPERSIONS OF VOLATILE COMPOUNDS OF FLUORINE AND BORON.

Carbon Tetrafluoride, Nitrogen Trifluoride, Fluoroform, Carbon-Nitrogen Compound of Fluorine $(CF_3N)_2$, Boron Hexahydride, and Nitrogenous Boron Hydride $B_3N_3H_6$.

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Received November 23, 1935.

(Communicated by Sir C. V. Raman, Kt., F.R.S., N.L.)

In an earlier communication,[1] the results of measurements of dielectric coefficients of the above-mentioned gases at different temperatures have been recorded. Simultaneous measurements of refractive indices and dispersions on the same specimens of gases were carried out, with a view to compare the electronic polarisations at long wave-lengths with the corresponding dielectric polarisations. From the data obtained, the atomic polarisations for these gases have been calculated as will be explained subsequently.

The apparatus, method of measurement, and the procedure adopted were practically the same as described in a separate communication by Watson and Ramaswamy.[2] One additional precaution to make sure of the zero reading of the compensator was taken. For this purpose the reading when both the gas tubes were empty was first taken, the gas was then introduced and fractionated if necessary and the bands counted until zero pressure in each case. The last stage of pressure reduction was done by slow condensation of the gas either by using a liquid air or a solid carbon dioxide bath. As in the earlier investigations,[2] low pressure counts for one or two other wave-lengths were made to enable easy computation of the total number of bands. All measurements were made at or nearly at the prevailing laboratory temperature.

The details concerning the methods of purification and the limits of purity have already been given in the earlier communication.[1]

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[1] K. L. Ramaswamy, *Proc. Ind. Acad. Sci.*, A, 1935, **4**, 364–377.

[2] H. E. Watson and K. L. Ramaswamy, "Refractive indices and dispersions of gases," (under publication).

Results.

Since details of calculation illustrating the accuracy of the results will be given in another communication,[2] it seems unnecessary to repeat them here. In the following tables I–VI, the values of $(n-1) \times 10^6$ (where n represents the refractive index) calculated to 760 millimeters pressure and 25°·0 Centigrade and corrected for compressibility, have been given. Column 1 gives the wave-lengths $\lambda \times 10^{-8}$ in centimetres corrected to vacuum, 2 the

TABLE I.

Carbon tetrafluoride.

$\lambda \times 10^{-8}$	$(n-1)$ obs.	$(n-1)$ cal.	Difference	t, p_m and *comp.*
6440·24	440·87	440·87	0·0	
5462·25	442·58	442·53	+0·05	$t=27°·5$ *C.*
5087·23	443·46	443·44	+0·02	$p_m=342$ *mm.*
4801·25	444·29	444·28	+0·01	*comp.*$=0·66\%$
4359·56	445·94	445·94	0·0	

The dispersion for carbon tetrafluoride can be summarised by the Sellmeier formula $n-1 \times 10^6 = \dfrac{9·9384 \times 10^{27}}{(22759·6 \times 10^{27} - \nu^2)}$.

TABLE II.

Nitrogen trifluoride.

$\lambda \times 10^{-8}$	$(n-1)$ obs.	$(n-1)$ cal.	Difference	t, p_m and *comp.*
6440·24	436·73	436·75	−0·02	
5462·25	439·11	439·11	0·0	$t=27°·0$ *C.*
5087·23	440·43	440·42	+0·01	$p_m=403·5$ *mm.*
4801·25	441·66	441·63	+0·03	*comp.*$=0·67\%$
4359·56	444·00	444·01	−0·01	

The dispersion for nitrogen trifluoride is best expressed by the Sellmeier formula $n-1 \times 10^6 = \dfrac{6·8443 \times 10^{27}}{(15888 \times 10^{27} - \nu^2)}$.

TABLE III.

Fluoroform.

$\lambda \times 10^{-8}$	$(n-1)$ obs.	$(n-1)$ cal.	Difference	t, p_m and *comp.*
6440·24	433·33	433·34	−0·01	
5462·25	435·38	435·37	+0·01	$t=27°·0$ C.
5087·23	436·48	436·48	0·0	$p_m=334·0$ mm.
4801·25	437·51	437·52	−0·01	comp.$=0·77\%$
4359·56	439·52	439·55	−0·03	

The results of fluoroform are best expressed by the Sellmeier formula

$$n-1 \times 10^6 = \frac{7·8660 \times 10^{27}}{(18368·8 \times 10^{27} - \nu^2)}.$$

TABLE IV.

Carbon-nitrogen compound of fluorine $(CF_3N)_2$.

$\lambda \times 10^{-8}$	$(n-1)$ obs.	$(n-1)$ cal.	Difference	t, p_m and *comp.*
6440·24	997·52	997·47	−0·05	
5462·25	1002·51	1002·47	−0·04	$t=28°·5$ C.
5087·23	1005·25	1005·31	+0·06	$p_m=310·0$ mm.
4801·25	1007·80	1007·77	−0·03	comp.$=1·75\%$
4359·56	1012·81	1012·83	+0·02	

The results of dispersion are best summarised in the expression

$$n-1 \times 10^6 = \frac{16·9275 \times 10^{27}}{(17186·5 \times 10^{27} - \nu^2)}.$$

observed value of $(n-1) \times 10^6$, 3 the value calculated from the dispersion formula given at the end of each table, 4 the difference between the observed and the calculated values of $(n-1) \times 10^6$. In the last column are mentioned the actual temperature t of measurement in degrees Centigrade, the mean pressure p_m in each experiment and the compressibility of the gas investigated expressed as a percentage correction for a mean pressure of 380 millimeters or for a change of pressure from 0 to 760 millimeters.

TABLE V.

Boron hexahydride.

$\lambda \times 10^{-8}$	$(n-1)$ obs.	$(n-1)$ cal.	Difference	t, p_m and *comp.*
6440·24	810·53	810·53	0·0	
5462·25	818·22	818·32	−0·10	$t=25°·0$ C.
5087·23	822·70	822·63	+0·07	$p_m=202·5$ mm.
4801·25	826·65	826·66	−0·01	comp.=0·97%
4359·56	834·63	834·63	0·0	

The dispersion can be summarised in the Sellmeier form by the expression

$$n-1 \times 10^6 = \frac{7\cdot1942\times10^{27}}{(9092\cdot7\times10^{27}-\nu^2)}.$$

TABLE VI.

*Nitrogenous boron hydride.**

$\lambda \times 10^{-8}$	$(n-1)$ obs.	$(n-1)$ cal.	Difference	t, p_m and *comp.*
6440·2	1275·7	1276·0	−0·3	
5462·3	1291·4	1291·4	0·0	$t=24°·8$ C.
5087·2	1300·1	1300·0	+0·1	$p_m=8·5$ mm.
4801·3	1308·2	1308·0	+0·2	comp.=40·4%
4359·6	1323·7	1324·0	−0·3	

* *Tentative.*

The results are expressed by the Sellmeier formula

$$n-1 \times 10^6 = \frac{9\cdot0178\times10^{27}}{(7284\cdot3\times10^{27}-\nu^2)}.$$

The usual Sellmeier formula was employed to summarise the results of dispersions and in all cases a single term proved sufficient, *viz.*, $n-1 = c/\nu_0^2-\nu^2$, where c is a constant, ν_0 and ν are the free frequencies of the dispersion electrons in a molecule and of the incident radiations respectively.

The value of ν is obtained from the expression $\nu = \frac{V}{\lambda}$ where V is the velocity of light and λ the wave-length of the incident radiation.

The individual values call for a little comment. The two gases carbon tetrafluoride and nitrogen trifluoride have been previously examined[2] and the results given as somewhat provisional. The present value for carbon tetrafluoride is about 2·7 per cent. lower than the value previously given[2] and it may be mentioned that Klemm and Henkel[3] have obtained a value about one per cent. higher than the present value.

The case of nitrogen trifluoride is interesting. The value of refractive index for the mercury green line 5462 Å, obtained in the present investigation is about 0·9 per cent. lower than the figure given in an earlier communication.[2] If one assumes an impurity of about 2 per cent. of air in the present sample of gas, the discrepancy can be easily explained. But then a difficulty arises with regard to the value of the dielectric coefficient, which according to this assumption should be about 1256 (calculated from the value obtained with the previous sample of gas) as against the value of 1220 given in the previous paper.[1] It appears, therefore, that probably traces of other fluorides having nearly the same value of refractive index but differing widely in the values of dielectric coefficients, are generated in quantities depending on the method and conditions of preparations.[4]

For the other gases, measurements by other authors do not seem to have been made. It is necessary to mention that the values for the nitrogenous boron hydride are given with reserve and need further confirmation.

Electronic and Atomic Polarisations.

The wave-lengths at which the measurements of dielectric coefficients are measured, can be considered infinite compared with the wave-length of light employed in the measurements of refractive indices. If one considers the effect of radiations of very long wave-lengths on the refractive index, the Sellmeier expression approximates to the form $n-1 = \frac{c}{\nu_0^2}$, since ν becomes practically zero.

In the following table VII, the electronic polarisations (represented by P_E) have been calculated using the Lorenz-Lorentz relation $\frac{n^2-1}{n^2+2} \cdot \frac{M}{D} = P_E$, and the values of $n_\infty - 1$ obtained as explained above. Since $\frac{M}{D}$ is the molecular volume which for an ideal gas is 22·412 litres at N.T.P. and $n^2 + 2$

[3] W. Klemm and P. Henkel, *Zeit. Anorg. und Angew. Chem.*, 1933, **213**, 115–125.

[4] Otto Ruff and L. Staub, *Zeit. Anorg. Allgem. Chem.*, 1931, **198**, 32-8.

for most gases is not far from 3, the value of PE at 25° ·0 Centigrade is easily obtained by multiplying $n_\infty^2 - 1$ by the factor ·008155. The correction when n^2+2 exceeds 3, has been made wherever necessary.

In column 2, the values of distortion polarisation PD (represented by A in the Debye's equation) given in the previous paper[1] are reproduced. The columns 3 and 4 give the electronic polarisation PE and the atomic polarisation PA (the difference between PD and PE) respectively.

TABLE VII.

Values of PD, PE, PA.

Substance	PD	PE	PA
Carbon tetrafluoride ..	9·72	7·12	2·60
Nitrogen trifluoride	9·08	7·03	2·05
Fluoroform	8·86	6·98	1·88
Compound $(CF_3N)_2$	21·35	16·06	5·29
Boron hexahydride	14·46	12·91	1·55
Nitrogenous boron hydride* ..	23·76	20·18	3·58

* *Tentative.*

Discussion.

The figures given in Table VII definitely indicate that the atomic polarisations in the case of all fluorine compounds investigated, are surprisingly large being about 30 per cent. of the corresponding electronic polarisations.

No clear relationship can be traced between molecular structure and atomic polarisation. It may be mentioned that the data from a systematic study of both dielectric and optical polarisations, are not sufficiently extensive for attempting to establish any relationship between PA and PE, although it is generally known that PA increases with the size of the molecule.

It has been the usual practice in the approximate calculations of dipole moments, to take PA as 10–12 per cent. of PE. This, however, will not be far from correct when the moment is sufficiently large, say of the order of one or more Debye units. From the results given in this communication, it appears that such an assumption is not applicable to the case of fluorine compounds and complex compounds of boron.

It is, therefore, intended to extend these investigations to more compounds and then critically examine the results to see if any definite relationships can be traced.

Summary.

1. The refractive indices and dispersions of carbon tetrafluoride, nitrogen trifluoride, fluoroform, nitrogen-carbon compound of fluorine $(CF_3N)_2$, boron hexahydride and nitrogenous boron hydride $B_3N_3H_6$, have been measured at the ordinary temperature using a Zeiss Interferometer of the Rayleigh type.

2. The compressibilities of the gases mentioned have been determined by studying the variation of refractive index with pressure.

3. The atomic polarisations of these molecules have been calculated from the dielectric and optical polarisations. It has been found that the fluorine compounds and the complex compound of boron $B_3N_3H_6$, have appreciable values of atomic polarisations.

Conclusion.

In conclusion I wish to acknowledge my indebtedness to Prof. Dr. Otto Ruff, Breslau, and to Prof. Dr. Alfred Stock, Karlsruhe, for the gift of the fluorine and boron compounds respectively. My grateful thanks are due to Prof. Sir C. V. Raman, Kt., F.R.S., N.L., for his kind encouragement and keen interest in the work.

DETERGENCY OF SOAP SOLUTIONS.

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and
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Received November 18, 1935.

Much work has been done on attempts to relate the cleansing power of a soap solution with its other properties, for example, surface tension, pH, etc. The object of the present work is to determine whether a relation exists between the amount of soap adsorbed under standard conditions by cotton, and some of the other properties of the solution which are considered to be related to the cleansing power. To measure the quantity of soap adsorbed by cotton a new technique has been devised and a value termed "the maximum efficient adsorption" determined. This value has been measured for a number of commercial house-hold soaps and for soaps prepared from vegetable oils and from pure fatty acids. The effect of the addition of various builders on the adsorption has also been studied. The maximum efficient adsorptions obtained have been compared with the pH value of the solutions and the drop numbers.

The results indicate that the maximum efficient adsorption is high with commercial soaps which are known to be good cleansing agents and to give satisfactory values for pH and surface tension. With simple soaps, which are known to be not so satisfactory as the commercial soaps, the adsorption figure is low and the values as regards pH and surface tension are unsatisfactory.

Experimental Methods.

The yarn selected was from Egyptian cotton of an average count of 80, with 30 turns per inch and an average test of 26 lbs. It was specially made to order and a bundle of 10 lbs. bought and every hank tested to satisfy the above specifications.

The yarn was boiled for three hours in 3% caustic soda and 10% soda-ash solution to free it from pectinous and fatty matters and from mineral oils acquired in spinning, and was then rinsed with water and washed with 0·5 % hot soap solution and again thoroughly rinsed with several portions of distilled water, wrung and dried in air.

7 to 7·5 gms. of the scoured and air-dried yarn was kept at 50° C. in an air-thermostat in an atmosphere of constant humidity, obtained by covering the inside walls of the thermostat with canvas saturated with water by spraying at intervals. After three hours, the yarn was removed to a desiccator and dried over calcium chloride for 24 hours. It was then weighed and immersed for fifteen minutes in a cylindrical jar containing one litre of the soap solution under test kept at 40° C. in an air-thermostat. Increase in the time of immersion did not affect the results.

To avoid curling of the yarn and to ensure complete immersion in the soap solution the hank was doubled and one end held by a hook supported by a glass rod resting on the mouth of the jar with the other end loaded with a weight of 50 gms. to keep the yarn in constant tension. At the end of the fixed time the yarn was removed from the jar and the excess of the solution allowed to drain by hanging the hank on a support under a tension of 250 gms. After the yarn was drained and air-dried, it was again exposed for three hours at 50° C. in the humid chamber and desiccated over calcium chloride for 24 hours and weighed. The increase in weight due to the adsorption of soap was noted and the results calculated to 10 gms. of the dried yarn.

Exposure to an atmosphere of constant humidity before and after immersion in the soap solution is essential to obtain consistent results.

The pH value was determined with Hellige's comparator by the indicator method and the surface tension by the drop number method using Traube's stalagmometer.

Experimental Results.

The above experiments were conducted with various commercial household soaps, with neutral sodium-soaps prepared from mowhra and cocoanut oils and also with the sodium salts of pure oleic and stearic acids. The effect of the addition of various builders to these salts was also examined.

To obtain the optimum temperature and time required for maximum adsorption, experiments were conducted with sodium oleate for concentrations ranging from 0·1 to 0·7% of anhydrous soap, (1) by keeping the temperature and concentration constant and varying the time, and (2) by keeping the time and concentration constant and varying the temperature. It was found that the optimum temperature and time for maximum adsorption was 40° C. and 15 minutes respectively; accordingly all experiments were performed at 40° C. and the yarn immersed in the soap solution for 15 minutes.

This result is in agreement with the recent experiments of Herites on his Congo-ruby number[1] and also with the washing experiments of Rhodes and Brainard.[2]

Commercial House-hold Soaps.

The following is the analysis of the commercial house-hold soaps employed :—

	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6
Moisture ..	27·1	27·75	49·28	28·1	35·1	36·2
Fatty acids ..	63·34	61·08	39·68	60·5	45·4	44·8
Free alkali ..	0·08	0·21	0·08	0·2	0·6	0·2
Combined alkali ..	9·30	8·94	5·32	9·0	6·9	6·6
Free fat and unsaponifiable matter ..	0·02	0·56	0·04	0·5	2·2	0·7
Other salts and glycerine (by difference) ..	0·16	1·46	5·60	1·7	9·8	11·5

It will be seen from Fig. 1 that the commercial soaps give an adsorption of about 0·1 gm. at a concentration of 0·5% of anhydrous soap. Further increase in concentration does not improve the adsorption so that the figure 0·1 is termed the "maximum efficient adsorption". The pH values of four of the six commercial soaps examined are steady at about 9·5 in the concentration range usually employed in practice, and this pH has been shown by the experiments of Zakarias[3] to be well adapted for washing purposes. Four of the soaps give a steady drop number in the practical range of 60, with the apparatus used. Soaps 1, 2 and 4 which give the highest adsorption, give a steady pH value of 9·5 and the highest drop number.

Fig. 2 shows similar experiments with mixtures of mowhra and cocoanut and of oleate and stearate soaps. Mixtures of mowhra and cocoanut soaps are known to be inferior as washing agents to the blended commercial soaps and they give a lower maximum efficient adsorption of 0·08. The pH values are not steady and the drop numbers are on the whole lower. The same remarks apply to mixtures of oleate and stearate. It will be noticed that mixtures of 25% mowhra and 75% cocoanut and 80% oleate and 20% stearate give the highest adsorption and drop number.

[1] *Z. Phys. Chem. Seinfenforsch*, 1929, Heft. 2.

[2] *J. Ind. Eng. Chem.*, 1929, **21**, 60.

[3] *Colloid Chemistry*, Alexander, **4**, 653.

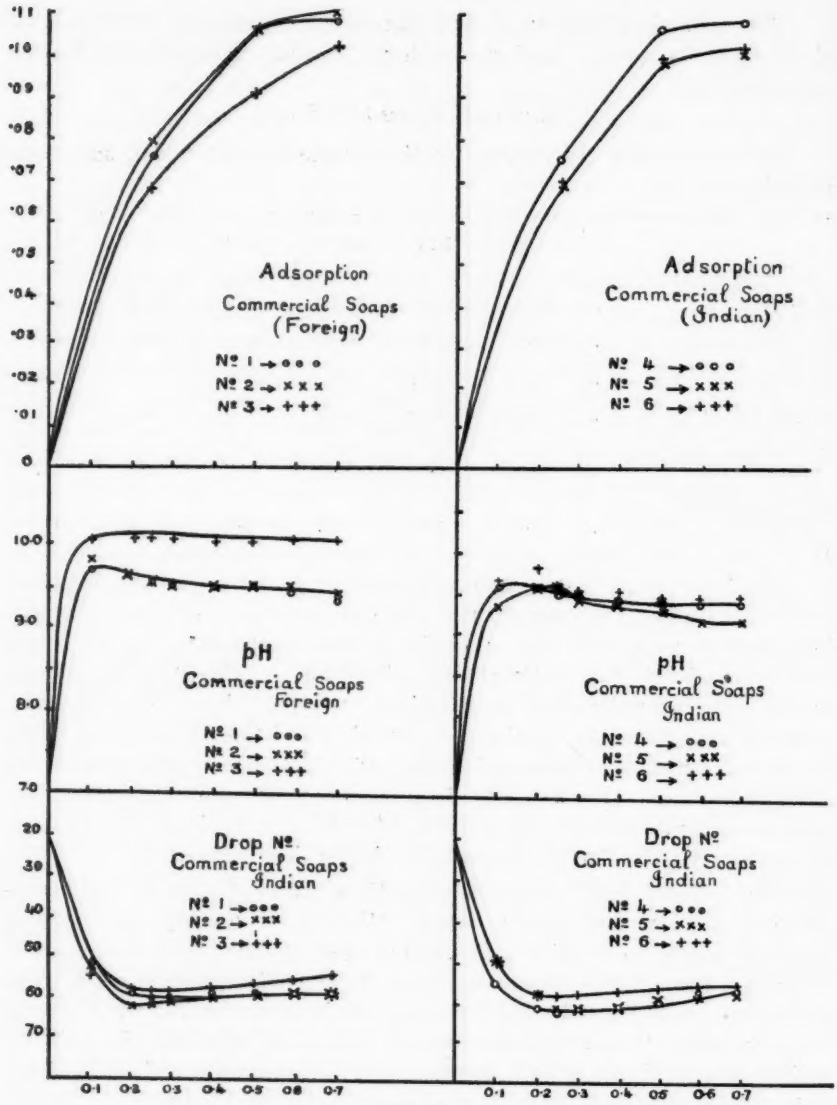
Adsorption
Commercial Soaps
(Foreign)
№ 1 → ooo
№ 2 → xxx
№ 3 → +++
Adsorption
Commercial Soaps
(Indian)
№ 4 → ooo
№ 5 → xxx
№ 6 → +++
pH
Commercial Soaps
Foreign
№ 1 → ooo
№ 2 → xxx
№ 3 → +++
pH
Commercial Soaps
Indian
№ 4 → ooo
№ 5 → xxx
№ 6 → +++
Drop №
Commercial Soaps
Indian
№ 1 → ooo
№ 2 → xxx
№ 3 → +++
Drop №
Commercial Soaps
Indian
№ 4 → ooo
№ 5 → xxx
№ 6 → +++
0·1 0·2 0·3 0·4 0·5 0·6 0·7

FIG. 1.

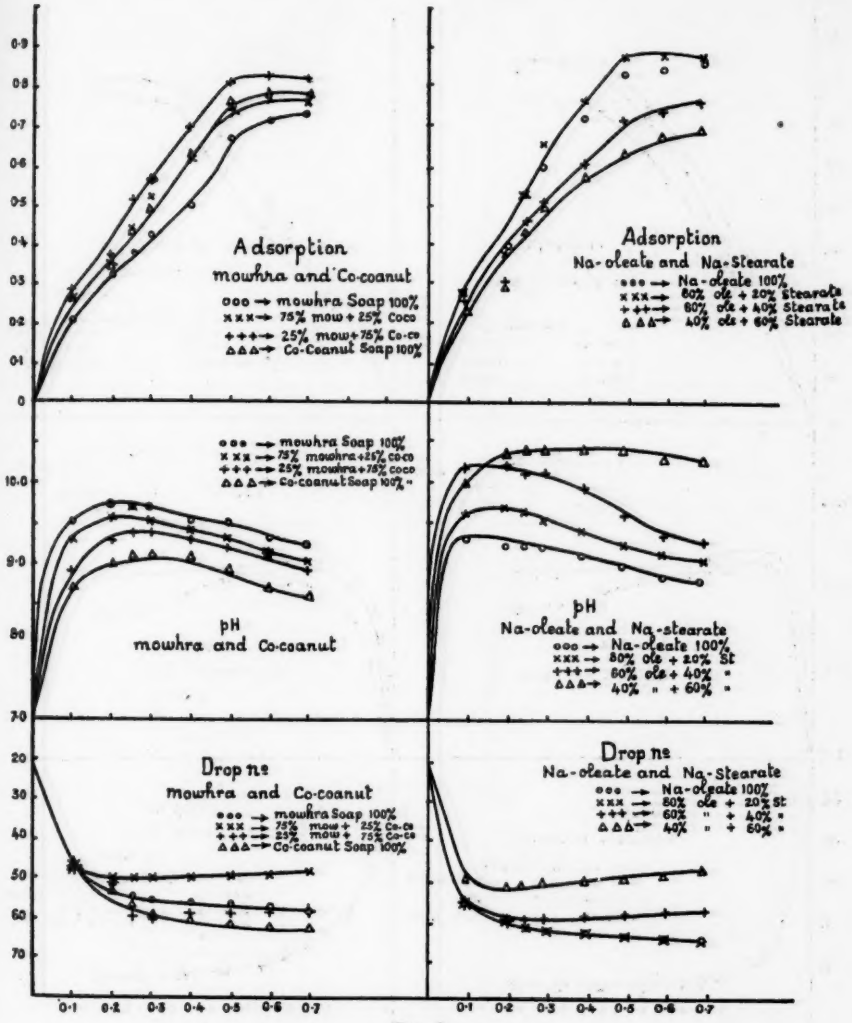

FIG. 2.

The adsorption figures are given in gms. $\times 10^{-1}$.

Fig. 3 shows the effect of addition of sodium hydroxide as a builder to oleate and cocoanut soaps. With sodium oleate addition of 0·1 to 0·5% hydroxide (calculated on the fatty acids contained in the soap) gives an improved adsorption; the drop number and the pH values are not affected. With cocoanut soap, the adsorption is not affected by addition of up to 0·5%

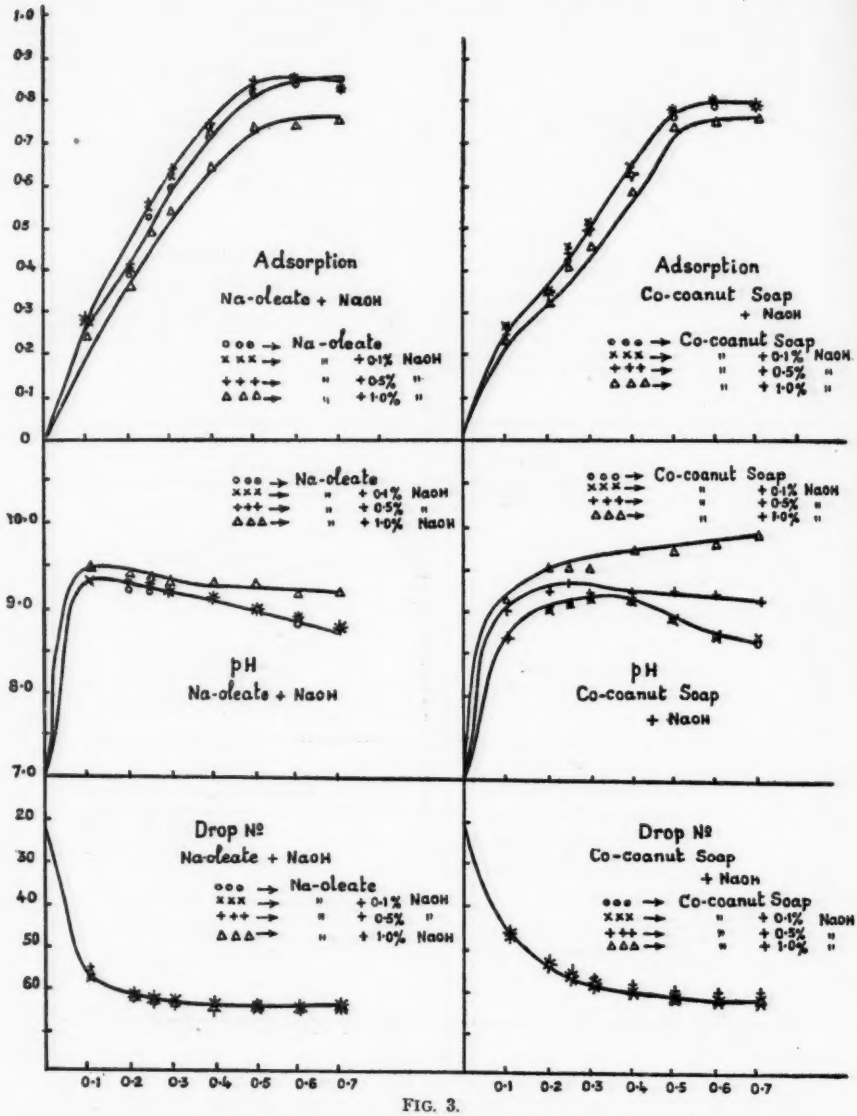

FIG. 3.

The adsorption figures are given in gms. $\times 10^{-1}$.

hydroxide ; the drop number is slightly raised and the pH value is improved. In practice it is found that addition of 0·1 to 0·5% hydroxide gives improved detergent effects.

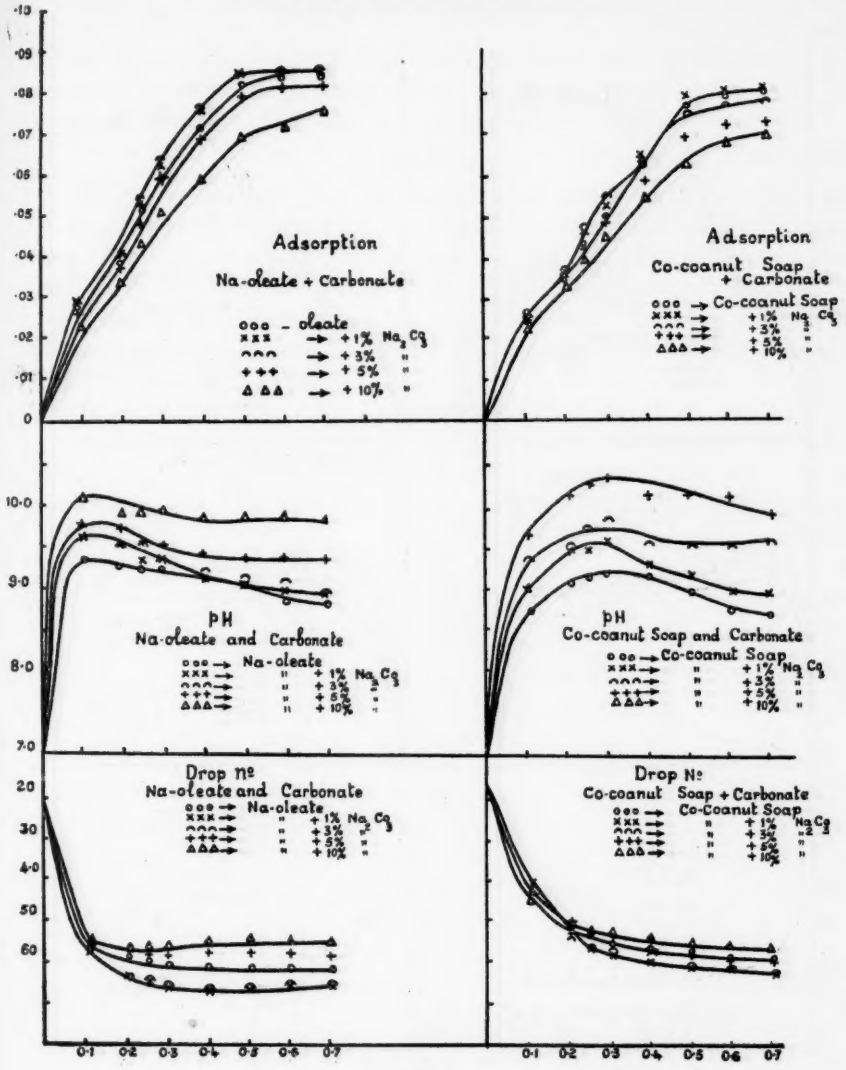

FIG. 4.

Fig. 4 shows the effect of addition of sodium carbonate to oleate and cocoanut soaps. Addition of 1% of carbonate (calculated on the fatty acids contained in the soap) to oleate gives satisfactory values for adsorption and drop number but rather a low pH; addition of 3% improves the latter defect. With cocoanut soap addition of 3% carbonate gives favourable

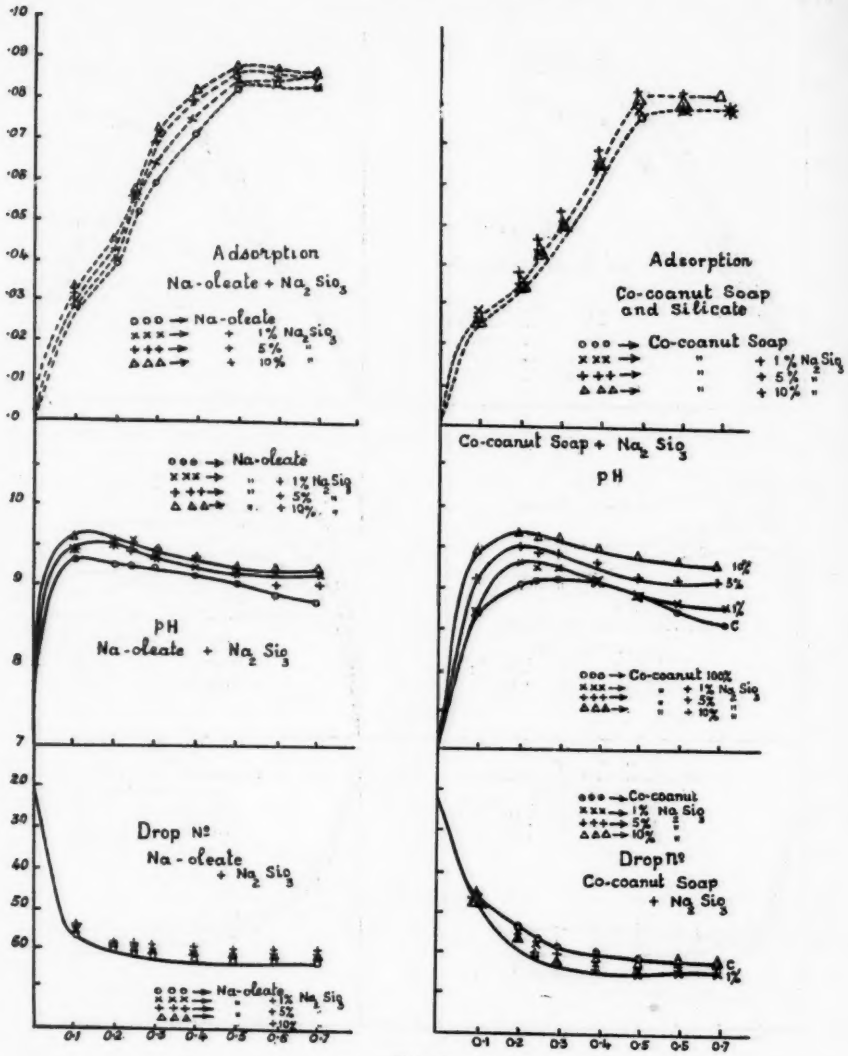

FIG. 5.

values of pH as well as drop number but the adsorption figure is not improved, 1% gives a better value. In practice 2 to 2·5% of carbonate is generally used.

Fig. 5 shows the effect of addition of sodium-silicate to oleate and cocoanut soaps. The adsorption in both cases increases with the addition of

silicate up to 10% (calculated on the fatty acids contained in the soap), the drop number is not greatly affected but the pH value is improved. In practice the amount of silicate used in house-hold soaps is up to 10%.

Conclusion.

It will be seen that from the experimental results described above that the conditions which are known to promote cleansing, also facilitate adsorption. From this it can be deduced that it is the soap adsorbed on the fibre that cleanses; the greater the quantity of soap adsorbed the greater the cleansing effect. The new adsorption test may, therefore, provide an accurate, though not a rapid, method for the comparison of the cleansing powers of a series of soaps.

Summary.

A method is described for measuring the adsorption of soap by cotton under standard conditions. Evidence is brought forward to show that the adsorption figure may be a measure of the detergent action of soap solutions.

UPLIFT PRESSURE ON WEIRS.

A Floor with a Line of Sheet Piles.

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Received November 20, 1935.

Introduction.

In two previous publications,[1, 2] an account has been given of the estimation of uplift pressure on weirs built on permeable foundations, by means of the potential distribution. The technique of the method has been described in the papers referred to above. It was definitely established in those papers, *that the law of subsoil flow is analogous to the distribution of potential which governs the flow of electricity in a conductor.* Having once established this fact, it became possible to employ the method to find the pressure distribution in any design of structure and to formulate laws for the various cases. The results are of immense practical importance for purposes of design. A knowledge of the uplift pressure under weirs is necessary, since, if they are not constructed to withstand the pressures, failures such as have occurred in the past may be repeated. Though the problem is extremely important from an engineering standpoint, yet these experiments offer a wide scope for theoretical research as well. The two cases dealt with in this paper are, a flush floor with different lengths of sheet pile at the upstream end, and a depressed floor with different lengths of sheet pile at the upstream end.

Results.

In the first series of experiments with a flush floor, the model was 12″ long and the lengths of the sheet pile were 1″, 2″, 3″, 4″, 5″ and 6″, thus giving the ratio of the floor length to sheet pile as 12, 6, 4, 3, 12/5, 2. This ratio is denoted by α in the paper.

(*a*) The pressure contours for the case when different lengths of sheet pile are introduced at the upstream end of a flush floor, maintaining the length of the floor constant, are given in Fig. 1. The different curves are for decrements of 5 % of the total difference of pressure between the upstream

and the downstream. In addition to these 5% lines, those indicating the percentage pressures at various important points, such as the end of the sheet pile and the beginning of the floor, are also marked in the figure.

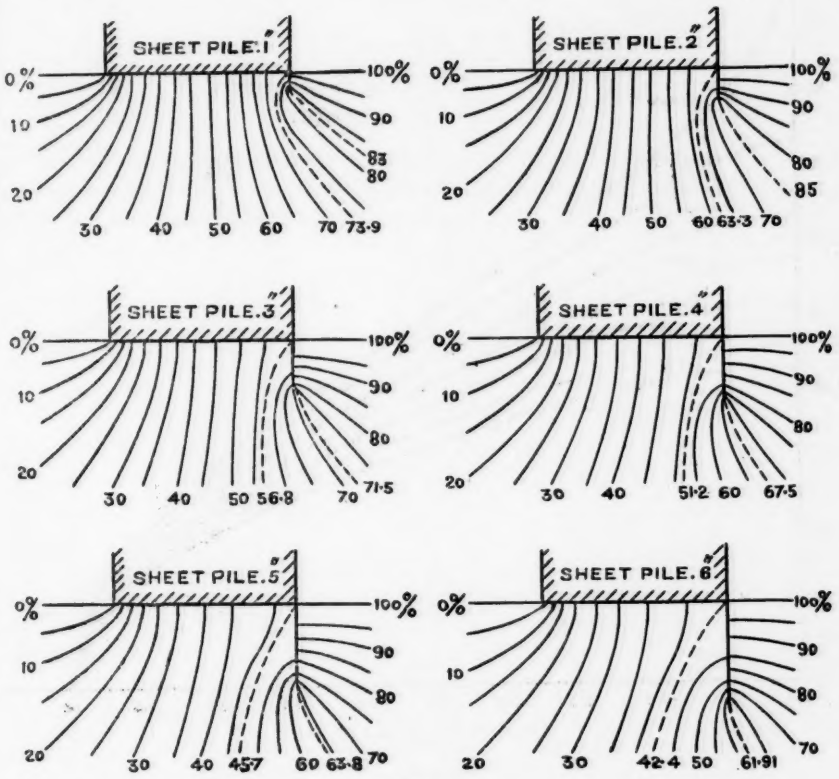

FIG. 1.

Pressure Contours—Flush Floor 12″.

(*b*) In Fig. 2 the percentage pressure along the floor is plotted against fractional distance for various values of α. By fractional distance is meant, the ratio of the distance from the beginning of the floor to the total length of the floor.

This case has been theoretically worked out by Prof. Weaver.[3] Fig. 2 shows also the comparison between the theoretical results according to Weaver and the experimental values. It is clear from this figure that theory and experiment are in accord.

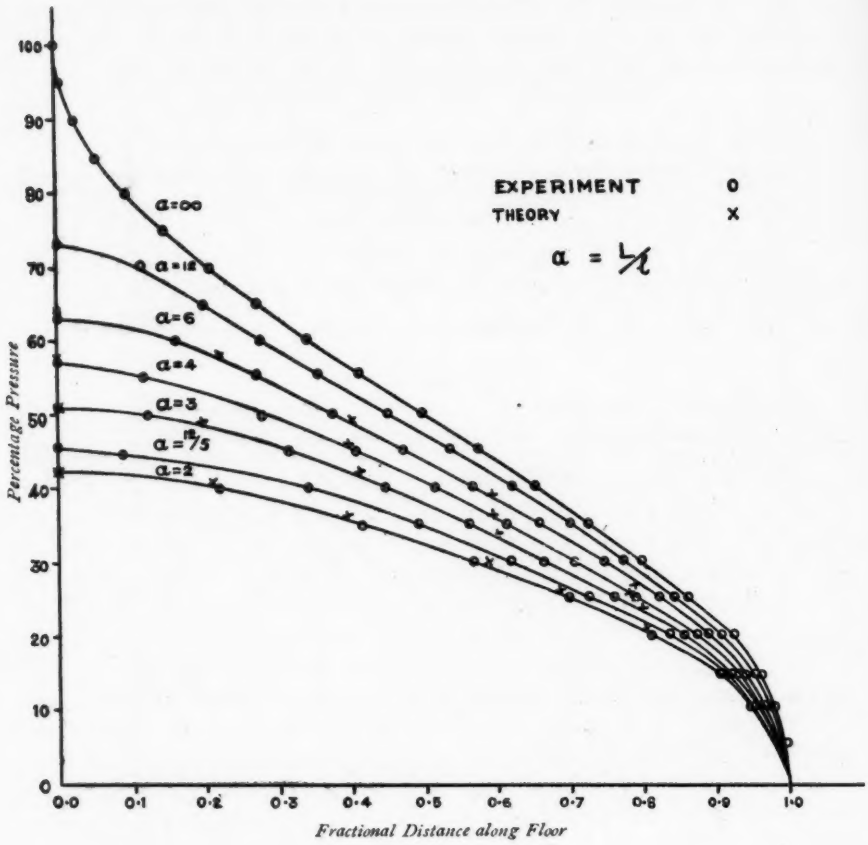

FIG. 2.
Pressure Distribution along Flush Floor.

(*c*) The variations of pressure at the points A and B of the structure for varying lengths of sheet piles are shown in Fig. 3. The corresponding values of α are also plotted along the abscissa. The positions of A and B are shown in the inset. The equations for these curves, giving the percentage pressure at A and B for any value of α, derived from theoretical considerations are[3]

$$\text{Cos}\left(\frac{\pi P_A}{100}\right) = \frac{1-\lambda}{\lambda}$$

$$\text{Cos}\left(\frac{\pi P_B}{100}\right) = \frac{2}{\lambda} - 1$$

$$\lambda = \frac{1 + \sqrt{1+a^2}}{2}$$

$$a = \frac{L}{l}$$

Here l is the length of sheet pile, and L, is the length of floor.
Pressures calculated according to these equations are also plotted in Fig. 3. They lie along the experimental curve.

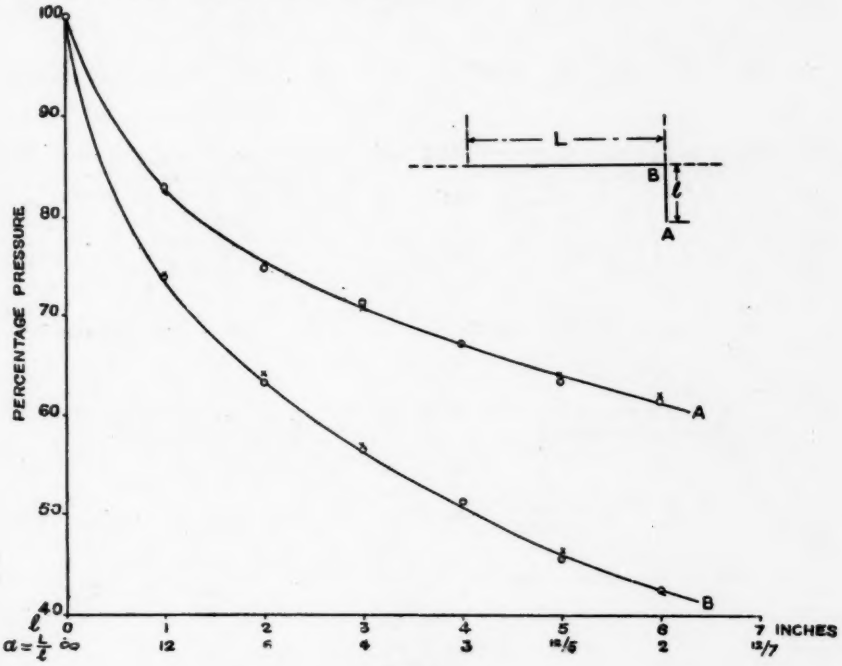

FIG. 3.
Pressures at A and B under Flush Floor.

It can be seen from this figure that to begin with, the curve is steep, gradually becoming flatter as a decreases. This means that unit increase in the length of the sheet pile, cuts off more pressure when the sheet pile is short, than when the sheet pile is long. In other words, the effectiveness of a sheet pile in cutting off pressure decreases with increase in length. A

chart is given in Tables I and II showing the pressure at A and B for various values of $\frac{1}{a}$.

(*d*) In the next series of experiments the floor of the model was 12″ in length and it was depressed by 2″, giving a ratio of depression to width, of $\frac{1}{6}$. With this floor, 6 sheet piles of different lengths as 1″, 2″, 3″, 4″, 5″ and 6″ were investigated thus giving values of α_1* ; as 12, 6, 4, 3, 12/5, 2.

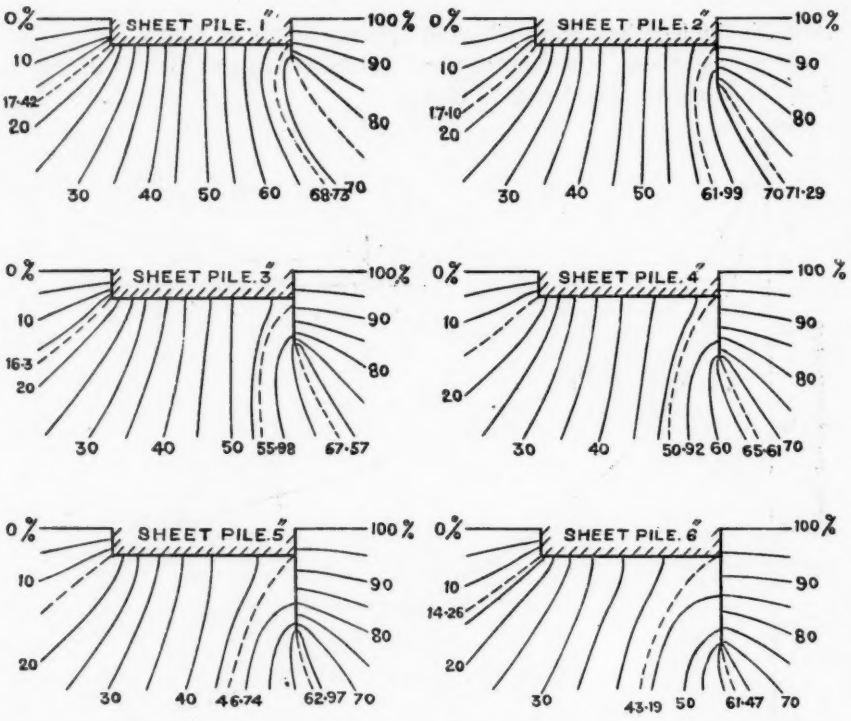

FIG. 4.

Pressure Contours—12″ Floor Depressed 2″.

The pressure contours for the six sets in this case are shown in Fig. 4. The lines are for decrements of 5% of the total difference of pressure between the upstream and the downstream. In addition to these, the lines at important points of the work such as the end of the sheet pile, the corner of the

* $\alpha_1 = \frac{L}{l_1}$ See inset in Fig. 6.

sheet pile and the floor, and the horizontal part of the depressed floor are also shown in the figure.

(*e*) The percentage pressure distribution along the floor in the depressed case is plotted against the fractional distance in Fig. 5, for various values of a_1*. This case is similar to that shown in Fig. 2 for the flush floor. The theoretical solution for the case of the depressed floor has not so far been obtained and hence, a comparison of the experimental with the theoretical is not possible at present.

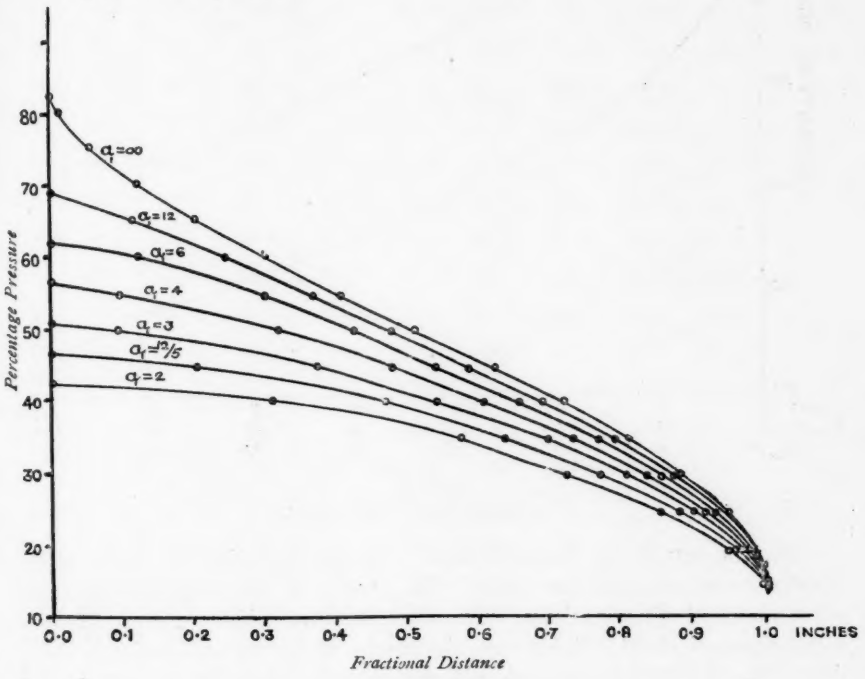

FIG. 5.

Pressure Distribution along Depressed Floor.

(*f*) In Fig. 6, the percentage pressure at A, B and on B–C are plotted as a function of the length of the sheet pile in the depressed case. For the position of the points A, B and C, see inset. A chart showing the values of P_A, P_B and P_{B-C} is given in Tables III, IV and V. The pressures at these points for any value of $\frac{l_2}{L}$ can be read from the chart, where l_2 is the length of the sheet pile including the two inches of the depression, and L is the length of the floor.

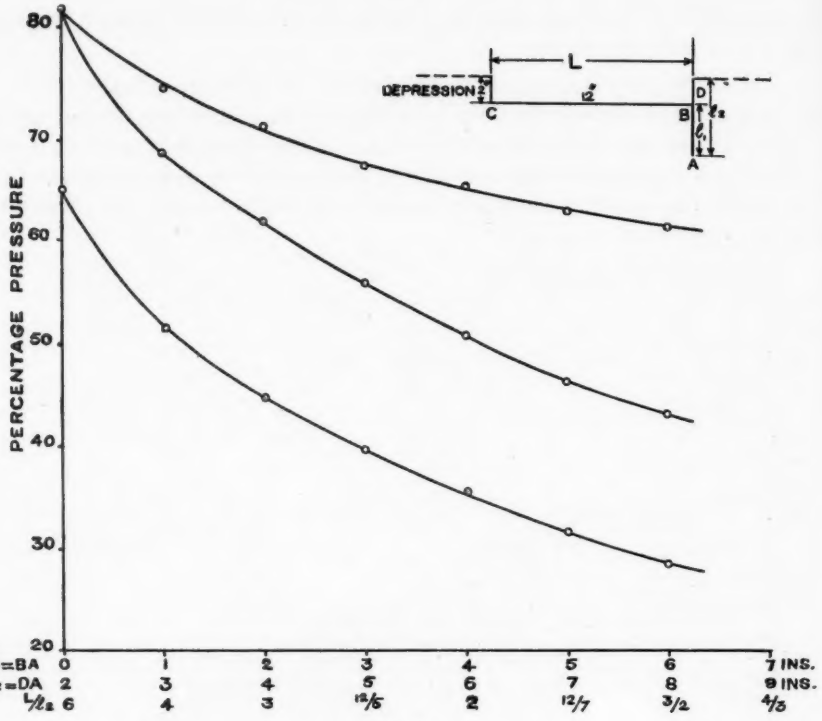

FIG. 6.

Pressures at A, B, and on B—C.

For the case of the depressed floor, a comparison with the values of the hydraulic method has been made. The results of the two methods agree when the sheet piles are long. But when the sheet piles are short, there is a difference of about 7% between the results of the two methods. This is due to the fact that in the hydraulic method, the sheet pile had a thickness of about half an inch which becomes comparable to the length of the pile when it is short. Also, the tubes inserted for measurement of pressures in the hydraulic method had a diameter of about quarter of an inch which becomes comparable to the length of the pile when it is short.

Summary.

The electrical method has been employed to determine the pressure distribution under models of weirs when different lengths of sheet pile have been introduced. One model had a 12″ flush floor and the lengths of the sheet piles introduced were 1″, 2″, 3″, 4″, 5″ and 6″. The complete systems

TABLE I. FLUSH FLOOR.

(See also Fig. 3.)

Table showing Values of P_A for Values of l/L
(Ratio of length of sheet pile to length of floor).

	·00	·01	·02	·03	·04	·05	·06	·07	·08	·09
·00	100·0	93·6	91·1	89·1	87·5	86·0	84·8	83·6	82·6	81·5
·10	80·6	79·7	78·9	78·1	77·3	76·6	75·9	75·2	74·6	74·0
·20	73·4	72·9	72·4	71·9	71·4	70·9	70·5	70·0	69·6	69·1
·30	68·7	68·3	67·9	67·5	67·2	66·8	66·5	66·1	65·8	65·5
·40	65·2	64·8	64·5	64·2	64·0	63·7	63·4	63·2	62·9	62·7
·50	62·5	62·2	62·0	61·8	61·6	61·4	61·2	61·0	60·8	60·6
·60	60·4	60·2	60·0	59·8	59·7	59·5	59·3	59·2	59·0	58·9
·70	58·7	58·6	58·4	58·3	58·2	58·0	57·9	57·8	57·6	57·5
·80	57·4	57·3	57·2	57·1	56·9	56·8	56·7	56·6	56·5	56·4
·90	56·3	56·2	56·2	56·1	56·0	55·9	55·8	55·7	55·7	55·6
1·00	55·5	55·4	55·3	55·3	55·2	55·1	55·1	55·0	55·0	54·9

TABLE II. FLUSH FLOOR.

(See also Fig. 3.)

Table showing Values of P_B for Values of l/L
(Ratio of length of sheet pile to length of floor).

	·00	·01	·02	·03	·04	·05	·06	·07	·08	·09
·00	100·00	91·3	87·4	84·5	82·1	80·0	78·1	76·5	74·9	73·5
·10	72·1	70·8	69·6	68·4	67·2	66·1	65·1	64·0	63·0	62·1
·20	61·2	60·3	59·4	58·6	57·8	57·1	56·4	55·6	54·9	54·2
·30	53·5	52·8	52·2	51·5	50·8	50·2	49·6	49·0	48·4	47·9
·40	47·4	46·8	46·3	45·8	45·2	44·8	44·3	43·8	43·3	42·8
·50	42·4	42·0	41·6	41·2	40·8	40·3	39·9	39·5	39·1	38·7
·60	38·3	37·9	37·6	37·2	36·8	36·5	36·2	35·8	35·5	35·2
·70	34·8	34·5	34·2	33·9	33·6	33·3	33·0	32·7	32·4	32·2
·80	31·9	31·7	31·4	31·2	30·9	30·7	30·4	30·2	29·9	29·7
·90	29·4	29·2	28·9	28·7	28·5	28·2	28·0	27·8	27·6	27·4
1·00	27·2	26·9	26·7	26·5	26·4	26·2	26·0	25·8	25·6	25·4

of equi-pressure lines and the variations of pressure at the ends of the sheet pile, and the corner of the sheet pile and floor are given in Figs. 1, 2, and 3. Charts showing the variations of pressure at the two latter points are given in Tables I and II. The theoretical equations obtained by Weaver, for the pressure distribution in the analogous cases, have been verified and are found to be in accord with the experimental results. Another model had a 12″ floor with a depression of 2″. Sheet piles of 1″, 2″, 3″, 4″, 5″ and 6″ were

TABLE III. DEPRESSED FLOOR.

(See also Fig. 6.)

Table showing the Values of P_A for Values of l_2/L (Ratio of length of sheet pile to length of floor).

	Ratio of depression to length of floor 1/6									
	·00	·01	·02	·03	·04	·05	·06	·07	·08	·09
·10								82·1	81·1	80·1
·20	79·2	78·3	77·5	76·8	76·1	75·4	74·8	74·2	73·6	73·0
·30	72·5	72·0	71·5	71·1	70·6	70·2	69·8	69·4	69·0	68·6
·40	68·2	67·9	67·5	67·2	66·8	66·5	66·2	65·9	65·6	65·3
·50	65·0	64·8	64·5	64·3	64·1	63·8	63·6	63·4	63·2	63·0
·60	62·8	62·6	62·4	62·2	62·0	61·9	61·7	61·5	61·4	61·2

TABLE IV. DEPRESSED FLOOR.

(See also Fig. 6.)

Table showing the Values of P_B for Values of l_2/L (Ratio of length of sheet pile to length of floor).

	Ratio of depression to length of floor 1/6									
	·00	·01	·02	·03	·04	·05	·06	·07	·08	·09
·10								81·4	78·9	77·0
·20	75·3	73·8	72·3	71·1	69·9	68·7	67·7	66·7	65·8	64·9
·30	64·0	63·2	62·4	61·6	60·9	60·2	59·5	58·8	58·1	57·4
·40	56·8	56·1	55·5	54·9	54·3	53·7	53·1	52·5	51·9	51·4
·50	50·8	50·3	49·7	49·2	48·7	48·2	47·7	47·3	46·8	46·4
·60	45·9	45·5	45·1	44·7	44·3	43·9	43·5	43·1	42·7	42·3

TABLE V. DEPRESSED FLOOR.

(See also Fig. 6.)

Table showing Values of P_{B-C} for Values of l_2/L (Ratio of length of sheet pile to length of floor).

	Ratio of depression to length of floor 1/6									
	·00	·01	·02	·03	·04	·05	·06	·07	·08	·09
·10								64·1	61·8	59·9
·20	58·2	56·7	55·4	54·2	53·0	52·0	50·9	50·0	49·1	48·2
·30	47·4	46·6	45·9	45·2	44·5	43·8	43·1	42·5	41·9	41·2
·40	40·6	40·1	39·5	38·9	38·3	37·8	37·2	36·7	36·2	35·7
·50	35·2	34·7	34·2	33·7	33·2	32·8	32·4	32·0	31·6	31·2
·60	30·9	30·5	30·2	29·9	29·6	29·3	29·0	28·8	28·5	28·3

fixed to this depressed floor and the pressure distributions at the end of the sheet pile, at the corner of the sheet pile and floor, and on the horizontal part of the masonry floor have also been investigated. The results are given in Figs. 4, 5, and 6. Charts showing the pressure distribution at the various points mentioned above are given in Tables III, IV, and V. With the help of the tables, it is now possible to determine the pressure under simple cases of weirs dealt with, and, hence, works can be designed to withstand the pressures. More complicated cases are under investigation.

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